CURRENT AND FUTURE PREDICTED ENVIRONMENTAL EXPOSURE TO ENGINEERED NANOPARTICLES

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Executive Summary

It is inevitable that during their manufacture and use, engineered nanoparticles (ENPs) will be released to the environment. This study was therefore performed to 1) identify the potential releases of ENPs to the environment; 2) review the fate of ENPs in environmental systems and 3) to assess the potential current and future environmental exposures.

Whilst ENPs may be emitted during the manufacturing process, the route of input to the environment will primarily depend on the end use of the ENP-containing product. In many of the applications, nanoparticles are in a fixed or bound form, and hence pose minimal risk to the environment. Applications that contain free engineered nanoparticles, and/or those that are likely to give rise to a greater likelihood and extent of exposure to the environment (e.g. airborne nanoparticles, or those products likely to be disposed of in wastewaters) include cosmetics, paints & coatings, catalysts & lubricants, water treatment and bioremediation products, food & food packaging, human and veterinary medicines and plant protection products. A number of products that contain ENPs have been identified that are currently on the UK market. However, due to a lack of published data, it is not currently possible to estimate the UK market penetration for these products. Moreover, whilst some data are available on the concentrations of ENPs in selected products, for some products this is totally lacking.

Available data indicate that, following release to water and air, nanoparticles will aggregate to some degree and that the behaviour of the resulting aggregates will be very different from the free nanoparticle The degree of aggregation and the size range of the aggregates is dependent on the characteristics of the particle, the concentration of the particles and the characteristics of the environmental system. ENPs will exhibit differing mobilities in the soils and waterbodies and in water treatment processes compared to their corresponding parent form. The behaviour of nanoparticles in environmental systems is therefore highly complex and appears to be dependent on not only the particle type but also the particle size and the nature of the receiving environments.

As a result of the lack of data on usage and environmental fate, a framework of simplistic models and algorithms for estimating concentrations in water, soil and air has been developed and applied to a range of ENPs. This modelling framework was applied to estimate the likely concentrations of ENPs in water and soil for a range of usage scenarios. For the 10% market penetration scenario, which probably overestimates current exposure levels, concentrations of silver, aluminium and fullerene C60 concentrations were predicted to be in the ng/l, whereas, titanium dioxide, zinc oxide, nanolatex and hydroxyapatite are predicted to be in the µg/l range (Table E.1). Predicted concentrations in soil ranged from <0.01 (cerium dioxide) to around 4.3 mg/kg (nanolatex). Predictions were also obtained for concentrations of selected ENPs in the air compartment. If, in the future, all of the product types investigated contained engineered nanoparticles, then concentrations in water could range from < 1 ng/l (cerium dioxide) to 1 mg/l (nanolatex).

The exposure data developed in this study provide a benchmark to a) inform the development of new analytical methodologies for environmental system, b) inform

the design of environmental fate studies; and c) interpret the significance of existing ecotoxicology data on ENPs. A comparison of the results of the exposure estimations with the available ecotoxicological data (Table E.1) is reassuring and indicates that even the conservative exposure concentrations generated in this study are many orders of magnitude lower than concentrations likely to cause acute effects in invertebrates, fish algae or sublethal effects on fish, invertebrates or bacteria.

Whilst this study has identified the potential environmental exposure arising from a range of key ENP types, the assessment has been limited by the availability of data and knowledge. Work in the future should therefore focus on 1) establishing a detailed knowledge of the content and use of products containing ENPs in the UK; 2) developing an understanding of the factors and processes affecting the fate and transport of ENPs in the environment; 3) the development and evaluation of more complex exposure assessment models; and 4) the development of a better understanding of the ecotoxicity of ENPs under environmentally-relevant exposure situations.

Table E.1. Summary of exposure and available effects data for selected ENPs in the UK environment (assuming 10% market penetration)

	Water (µg/l)	Soil (µg/kg)	Air (mg/m³)	Aggregate size (nm) in water mean and range	Invertebrate EC50 (µg/l)	Fish LC50 (µg/l)	Algae EC50 (µg/l)	Other endpoints
Ag	0.010	0.43	-	-	-	-	-	-
AlO₃	0.0002	0.01	-	-	-	-	-	-
Au	0.14	5.99	-	-	-	-	-	-
CeO₂	<0.0001	<0.01	6 x 10⁻⁷	-	-	-	-	-
fullerenes	0.31	13.2	-	75 (25-500)	> 35000	>>5000	-	effects on invertebrate behaviour at 260 µg/l; bacterial growth effected at 40 µg/l; bacterial phospholipids effected at 10 µg/l
hydroxyapatite	10.1	422	-	-	-	-	-	-
latex	103	4307	-	-	-	-	-	-
organo-silica	0.0005	0.02	-	-	-	-	-	-
SiO₂	0.0007	0.03	-	205 (135-510)	-	-	-	bacterial growth not effected at 500000 µg/l
TiO₂	24.5	1030	7	330 (175-810)	>100,000	>100,000	16,000	effects on invertebrate behaviour at 2000 µg/l; bacterial growth not effected at 100000 µg/l
ZnO	76	3194	-	480 (420 – 640)	-	-	-	90% bacterial growth not effected at 10000 µg/l

1. Introduction

Rapid developments in nanotechnology in recent years have already paved a way for a multibillion-dollar industry worldwide. The market impact of nanotechnology, a collective term used for a variety of scientific and engineering disciplines that deal with materials in the size range of up to 100 nanometres, is widely expected to reach 1 trillion US$ by 2015, with a global employment of around 2 million workers (Roco and Bainbridge, 2001). At present, the majority of manufacturing and use of nanomaterials occurs in the United States, followed by the European Union (EU), with its 30% share of this sector. Within the EU, the UK accounts for nearly a third of the sector (Chaudhry *et al.*, 2005; Aitken *et al.*, 2006). A study in 2005 identified around 50 companies in the UK involved in manufacture, processing, and/or use of nanomaterials in the UK (Chaudhry *et al.* 2005). Another similar number of organisations, including university departments, spin-offs, and private companies, is involved in nanotechnology-related R&D in the UK. The study has identified the main nanomaterials currently produced in the UK to include nano-powders (metals, metal oxides, alloys), magnetic nanomaterials, carbon nano-tubes, nano-ceramics, nano-silica, quantum dots (metal and semi-conducting nanocrystals), polymer nanocomposites, and nano-films. The nanomaterials manufacturing in the UK is weighted heavily towards bulk markets in metals and metal oxides, with some applications for niche markets such as quantum dots. The manufacturing also does not reflect the global emphasis on fullerenes, nanotubes, and nanofibres, and there is currently no commercial manufacturer of fullerenes in the UK. The study has also indicated that only a few sectors (e.g. paints and coatings, cosmetics, catalysts, polymer composites etc) are using nanomaterials in any significant quantities. However, with new and emerging applications and markets, this situation is likely to change in the future.

The current and projected applications of nanomaterials include catalysts, lubricants and fuel additives; paints, pigments and coatings; cosmetics and personal care products; medical, dental, drug delivery and bionanotechnology; functional coatings; hydrogen storage and fuel cells; nanoelectronics and sensor devices; optics and optic devices; security and authentication applications: structural (composite) materials, conductive inks and printing; UV-absorbers and free-radical scavengers; construction materials; detergents; food processing and packaging; paper manufacturing; agrochemicals, plant protection products and veterinary medicines, plastics, and weapons and explosives. A variety of consumer products that contain nanomaterials are already available in the UK and the EU. Examples of these include self-cleaning glass, anti-microbial wound dressing, paints and coatings, fuel catalysts and cosmetics (The Woodrow Wilson Nanotechnology Consumer Products Inventory www.nanotechproject.org/consumerproducts). Current market indicators also suggest that many more applications of nanotechnologies will emerge in consumer products in the coming years, impacting on every walk of life.

Such proliferation of nanotechnologies into consumer products has also raised a number of technological, health and safety, environmental, ethical, policy and regulatory issues. This is partly because of the properties of manufactured nanomaterials that may widely differ from the 'conventional' micro or macro- forms of the same materials. The concerns have also arisen from a growing body of scientific evidence that indicates that free nanoparticles can penetrate cellular

barriers, and that exposure to some forms of nanoparticle can lead to an increased production of oxyradicals and potential oxidative damage to the cell (Oberdörster, 2000; 2004; Donaldson *et al.*, 2002; 2004). Another major concern is that little is known about the impacts on the environment that may result from the release of nanomaterials, especially free nanoparticulate forms.

In 2004, a review carried out by Royal Society and the Royal Academy of Engineering highlighted a number of uncertainties and emphasised the need to increase our understanding of the human health and environmental risk posed by nanomaterials, in particular nanoparticles and nanotubes (The Royal Society and The Royal Academy of Engineering, 2004). The UK Government accepted these recommendations (HM Government, 2005), emphasising that while nanotechnology offers enormous benefits, the new technology needs to be properly regulated to safeguard the benefits as well as people and the environment. The strategy thus includes building a robust evidence base in the area of nanotechnologies exposure, hazard and risk assessment. Amongst the objectives set out by the Government's Nanotechnologies Research Co-ordination Group (NRCG) include assessment of sources of nanomaterials and their fate and behaviour in air, soils and water, and with a priority to evaluate current and future exposure to nanoparticles. This study has been carried out to collate existing knowledge on these issues and to identify gaps in knowledge that may need further research.

2. Objectives

The overall objective of this study was to evaluate the current environmental exposure arising from existing production, uses and disposal of engineered nanomaterials and to predict likely future exposures of nanomaterials in development. This was addressed using the following specific aims:

1. to identify current nanomaterials produced in the UK and their actual and predicted usage volumes (Chapter 3)
2. to identify new developments in the field of nanomaterials and to assess the potential for environmental contamination arising from these (Chapter 3)
3. to assess the likely fate and behaviour of nanomaterials in the environment (Chapter 4)
4. to determine the potential for exposure at all stages of nanomaterial production, use, disposal and recycling (Chapter 3)
5. to quantify current and potential concentrations of nanomaterials in the environment and assess the value of current models for predicting exposure (Chapter 5)
6. to identify work ongoing elsewhere of relevance to the study (Chapters 3, 4, 5, 6)
7. to recommend future research requirement (Chapter 6)

3. Current and future usage of engineered nanoparticles in the UK

The exposure of the environment to engineered nanoparticles is going to be determined by the way in which products containing nanoparticles are produced used and disposed of, the amount of a particle used within a product and the overall usage of the product. Therefore, in this Chapter we identify those product types that are likely to have the greatest potential for release of ENPs to the natural environment and attempt to determine product usage and composition.

3.1. Usage of engineered nanoparticles

The advent of nanotechnology in recent years has already led to a wide-ranging, multibillion-dollar global industry. The use of ENPs in a range of product types is predicted to increase over the coming years (Table 3.1) and the global market impact of nanotechnology is expected to reach 1 trillion US$ by 2015, with around 2 million workers (Roco and Bainbridge 2001). Whilst the majority of manufacturing and uses of nano-scale materials, including nanoparticles and nanotubes (collectively termed as nanomaterials in this report), occur in the United States, the European Union (EU), with its 30% global share of this sector, is not lagging far behind. Within the European Union, the UK accounts for nearly a third of the market (Chaudhry *et al.*, 2005).

A study in 2005 found that around fifty companies in the UK were involved in manufacturing, processing, and/or applications of nanomaterials, with a similar number of non-commercial organisations undertaking R&D (Aitken *et al.*, 2006). The main nanomaterials produced in the UK include nano-powders (metals, metal oxides, alloys), magnetic nanomaterials, carbon nano-tubes, nano-ceramics, nano-silica, quantum dots (metal and semi-conducting nanocrystals), polymer nanocomposites, and nano-scale films (Chaudhry *et al.*, 2005). A search of the Woodrow Wilson Nanotechnology Consumer Products Inventory showed 21 nanotechnology based consumer products currently available in the UK. They range from textiles, through anti-microbial wound dressings, paints and coatings, to fuel catalysts and cosmetics.

The other current and projected applications of nanotechnologies include remediation of contaminated soil and groundwater, coatings and pigments, construction materials, detergents, electrical and electronic equipment, food processing, food packaging, fuel cells and batteries, medical applications, paper manufacturing, plant protection products and agrochemicals, lubricants and fuel additives, veterinary medicines, drinking water treatment, and weapons and explosives (Chaudhry *et al.*, 2006).

In many of the applications, nanoparticles are in a fixed or bound form, and hence pose minimal risk to the environment. For this project, those applications were selected for study that pose a relatively high-risk of exposure. For example, those applications that contain free engineered nanoparticles, and/ or those that are likely to give rise to a greater likelihood and extent of exposure to the environment (e.g. airborne nanoparticles, or those products likely to be disposed of in wastewaters). The following applications were, therefore, identified and included in the study:

- Cosmetics

- Paints & coatings

- Catalysts & lubricants

- Water treatment

- Food & food packaging

- Human and veterinary medicines

- Plant protection products

The types of engineered nanoparticles either in use or expected to be used in these product categories are discussed below and the likely routes of release to the environment are discussed. Where available, information has been obtained on the concentrations of the ENPs in the product types and this is tabulated in table 3.2.

3.2 Cosmetics and personal care products

The information gathered so far indicates that cosmetics and personal care products represent the largest number of nanotechnology based consumer products currently available on the market. Within this sector, sunscreen preparations are the dominant application at the current time. The majority of these preparations contain inorganic nanoparticles of UV absorbers such as titanium dioxide (TiO_2), zinc oxide (ZnO) and iron oxides (Fe_3O_4, Fe_2O_3) (Table 3.2).

The nanoparticulate form of TiO_2 is used in sunscreens due to its ability to absorb and reflect UV light whilst appearing transparent to visible light, and is therefore more acceptable to the consumer. One example in the UK is Oxonica's Optisol®, which is incorporated in Boots Soltan® range of sunscreen products. Optisol® is a photostable UV absorber based on manganese-doped titanium dioxide, which is added to sunscreen preparations at around 5% concentration for enhanced UVA protection.

Cosmetics products, such as skin creams, containing fullerenes (carbon bucky balls) have recently appeared on the market. An example is Zelen's day and night skin creams with C60 fullerene, which is claimed to be 100 times more effective as an antioxidant than vitamin E (www.zelens.com/).

An emerging use of nanoparticles in cosmetics is that of nano-silver, which because of antimicrobial action is claimed to treat spots and acne. The addition of nano-silver in personal care products may, therefore, be considered as a medical use.

Table 3.1. Estimated global production volumes of various nanomaterials and devices (Royal Society 2004)

Application	Material/device	Estimated global production (tonnes per year)		
		2003-04	2010	2020
Structural applications	Ceramics, catalysts, composites, coatings, thin films, powders, metals	10	10^3	10^4–10^5
Skincare products	Metal oxides (titanium dioxide, zinc oxide, iron oxide)	10^3	10^3	10^3 or less
Information & Communication Technologies	Single wall nanotubes, nano electronics, opto-electro materials (titanium dioxide, zinc oxide, iron oxide), organic light-emitting diodes (OLEDs)	10	10^2	10^3 or more
Biotechnology	Nanoencapsulates, targeted drug delivery, bio-compatible, quantum dots, composites, biosensors	less than 1	1	10
Instruments, sensors,	MEMS, NEMS, SPM, characterisation dip-pen lithography, direct write tools	10	10^2	10^2–10^3
Environmental	Nanofiltration, membranes	10	10^2	10^3–10^4

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Another major use of nanomaterials in cosmetics is that for anti-ageing skin care products. The nanocapsules, or self-assembled nanostructures, e.g. nanosomes are claimed to allow absorption of nano-ingredients into the skin more readily than conventional sized materials. Examples include nanoencapsulated vitamin E, ceramides. Nano gold has also recently been included in anti-ageing creams and facemasks. A variety of other uses of nanotechnology in cosmetics is expected in the coming years.

Data have not been found on the amounts of nanomaterials in use in the cosmetics sector, however information is available on total usage volumes for all cosmetics. For example, the overall cosmetic & toiletry chemicals market in the USA in 2005 has been estimated at 5,860 million US$, with an average yearly growth of 5.84% (Source: The Freedonia Group, Inc). This includes surfactants (1450 million US$), aroma chemicals & blends (845 million US$), fat-based products (810 million US$), natural products (710 million US$), and other products (2045 million US$).

The manufacture and formulation of cosmetics and personal care products is likely to result in emissions to air, water, land and waste. It can be assumed that the main use of cosmetics will be by consumers and that this would result in emissions to the aquatic environment. Sunscreen and other cosmetics applied on skin may enter surface waters directly during swimming or bathing, or indirectly through sewerage systems during washing or showering. Waste cosmetics are most likely to be disposed of in household waste that may be land filled or incinerated. From the current knowledge of nanotechnology applications for cosmetics and personal care products, the most likely nanomaterials entering the aquatic environment will be titanium dioxide, zinc oxide, iron oxide, fullerenes, nanosilver, nanogold and certain organic nanosomes.

3.3. Catalysts, lubricants and fuel additives

The main current applications of nanomaterials in transport, specifically road transport, relate to the use of catalysts, lubricants and fuel additives. These applications are claimed to reduce fuel consumption and particulate emissions. For example, Oxonica's Envirox™ is a nano cerium oxide based fuel borne catalyst that is added to diesel at a concentration of 5-10 ppm and is claimed to increase fuel efficiency by ~10%. The catalyst is already in use on a large scale in bus fleets in a number of countries including the Philippines, New Zealand. Another example is the use of platinum nano-composite catalysts for vehicle emission controls.

The overall demand for chemical catalysts in the USA in 2004 was estimated at 1,030 million US$, with an average yearly growth of 3.05% (Source: The Freedonia Group, Inc). The demand for lubricants in the USA in 2005 was estimated at 2.7 billion gallons (Source: The Freedonia Group, Inc). This includes engine oils (51% = 1.377 billion gallons), process oils (18% = 0.489 billion gallons), general industrial oils (12% = 0.324 billion gallons), and other (19% = 0.513 billion gallons).

The manufacture and formulation of nanotechnology based catalysts, lubricants and fuel additives may result in emissions to air, water, land or waste. The use of fuel in vehicles could result in direct aerial emission of nanoparticles through vehicle exhaust. It is also estimated that around 50% the engine oil is lost from manufacturing to disposal stages due to evaporation, usage, spillages etc. It is likely that, during consumer use, some fuel and oil may also reach the sewerage system

from surface run-off. Waste lubricants are most likely to be disposed of as special waste that may be land filled or incinerated. From the current knowledge of nanotechnology applications for catalysts, lubricants and additives, the most likely nanomaterials entering the aquatic environment will be cerium oxide.

3.4 Water treatment and bioremediation

ENPs may be used in water treatment or for the remediation of contaminated soils. For example, polymeric nano-network particles may be used in soil and groundwater remediation (Masciangiloi & Zhang, 2003; Tungittiplakorn *et al.* 2004). Zero-valent iron (ZvFe) has been suggested for remediation of soils and groundwaters (e.g. O'Hara *et al.*, 2006). ZvFe can remove aqueous organic contaminants such as chlorinated solvents by reductive dechlorination and aqueous metal ions by reduction to an insoluble form (Ponder *et al.*, 2000). Stabilised iron phosphate nanoparticles have been shown to reduce the leachability and bioaccessibility of lead in soils. ZnO and TiO_2, and bimetallic particles such as iron/palladium, iron/silver and Zn/palladium may also be used in soil remediation technologies (Masciangiloi & Zhang, 2003; Mahmoodi *et al.*, 2007). Metal oxide particles such as ZnO and $ZnWO_4$ are activated by light and can act as photocatalysts for treatment or organic contaminants such as chlorinated phenols (Huang *et al.*, 2007) whilst TiO_2 has been tested for its oxidative and reductive transformations of organic and inorganic contaminants in air and water (Kamat & Meisel, 2003; Mahmoodi *et al.*, 2007; Klupinski *et al.*, 2004; Klongdee *et al.*, 2005).

The use of nanoparticles in treatment of polluted soil and water is likely to result in emissions to surface and ground water, although in many cases the nanoparticles will be immobilised thus reducing the potential for release to the environment (e.g. Mahmoodi *et al.*, 2007). From the current knowledge of nanotechnology applications for water treatment, the most likely nanomaterials entering the environment will be iron, silica, palladium and organic nanoparticles such as polyurethane.

3.5 Paints & coatings

The nanomaterials used in paints and coatings are generally those that have already been used in conventional forms, e.g. titanium dioxide and silica. The typical components in paints and coatings include pigments, extenders, binders, thinners, solvents and additives. A wide variety of coatings is available that are designed for specific purposes; e.g. scratch-resistance, ease of cleaning, dirt-repellent, antimicrobial activity etc. Nanomaterials have also been used as additive in printing inks. The use of nanoparticles for the controlled release of biocides in solid wood coatings has also been explored (e.g. Liu *et al.*, 2001).

Advantages of nanotechnology based paints and coatings include reduction in the amount of materials and solvents, extended life of paints and coatings that reduces the frequency of re-coating. Examples include BASF's Laromer™ PO9026V range of polyether acrylate with 50 % nano-scale silica for UV-curing coatings. The acrylic resin is claimed by the manufacturers to have extraordinarily good resistance to scratching and can be used in formulations with other radiation curable coatings for wood, wood products and plastics. Scratch resistance of coatings can be improved

dramatically by adding approx. 30 % (by weight of the recipe) of Laromer® PO 9026 V (i.e. 15% of nanosilica) (www.basf.com/rawmaterials/pdfs/PO9026V.pdf).

Other potential uses of nanomaterials in coatings include use of UV absorbers to help prevent UV degradation of coatings; use of nano-silver in paint for indoor and outdoor wood structures to prevent mould and fungal damage; dirt-repellent coatings (e.g. Pilkington's self-cleaning glass coated with a nano-layer of titanium dioxide); barrier and antimicrobial coating for food packaging, and coatings for inside of drinking water pipes. The use of nanomaterials in inks is currently focused on anti-counterfeiting marking, by incorporating fluorescent semi-conducting nanocrystals or quantum dots, or conductive or magnetic nanomaterials into ink for ink-jet printing.

The Western European paint and coatings market is estimated at 6.430 million tons in 2004 (source: Information Research Limited). The applications of paints and coatings include decorative (62%), general industrial (10%), wood finishes (6%), powder coatings (5%), coil coatings (3.5%), protective coatings (3%), automotive OEM (2.5%), marine paints (2%), vehicle refinishes (2%), coatings for plastic (2%), can coatings (1%), radcure coatings (1%) (Source: Information Research Limited).

The global paints and coatings market stands at an estimated 29.4 million tonnes, with an average yearly growth of 2.6% (source: Datamonitor). It can be estimated that major applications of paints and coating will be for decorative (18.23 million tonnes), general industrial (2.94 million tonnes), wood finishes (1,76 million tonnes) and powder coatings (1.47 million tonnes).

3.6 Food and food packaging

There is some evidence that nanomaterials are being incorporated into food and health food products; at present it is likely that this only occurs outside the UK. However, many food companies are currently investing in nanotechnologies. Future uses may include changing the structure, colour and/or flavour of food products. Nanotechnology derived food packaging materials are the largest category of current nanotechnology applications for the food sector.

The overall nanofood market (including packaging) has been estimated at US$7 billion in 2006, and will reach US$20.4 billion by 2010 (Source: Helmut Kaiser Consultancy). Another report has estimated food applications of nanotechnologies in 2006 to be around $410m (food packaging US$210m, food processing US$100m, food ingredients US$100m) (Source: Cientifica 2006). This report has estimated that by 2012 the overall market value will have reached $5.8 billion (food packaging $2930m, food processing $1303m, food ingredients $1475m, and food safety $97m). The most likely nanomaterials entering the environment through disposal of food packaging will be clay, and silver nanoparticles.

3.7 Nanomedicines

There are over 75 drugs, delivery systems, diagnostic tests and devices related to cancer and over 55 related to drug delivery in general. In both cases, it is evident that the vast majority of items are in the early stage of development or preclinical testing phases.

3.8 Pesticides

Potential ENP containing agrochemicals include fullerene fertiliser containing ammonia, the application of iron nanoparticles to help seed germination and the use of nanotechnologies as soil binders (www.azonano.com). Nano-encapsulation and solid lipid nanoparticles have also been explored for the delivery of agrochemicals (e.g. Frederiksen *et al.*, 2003). These substances could be directly applied to soils and may also enter aquatic systems through spray drift. Ecotoxicity data for lipid nanoparticle formulations of the pesticide gamma-cyhalothrin indicate that the particles reduce the effect of the pesticide on aquatic organisms (Frederiksen *et al.*, 2003).

3.9 Summary

1. Engineered nanoparticles have the potential to be used in a wide range of product types and the amount used is anticipated to increase over the coming years. It is inevitable that during the use of these products ENPs will be released to the environment.
2. The release of ENPs to the environment will be dependent on the amount of a particular product used, the pattern of usage and the concentration of the ENP within a product. Whilst ENPs may be released during the manufacturing phase, it is believed that the major route of input to the environment will depend on the end-use.
3. ENPs may be contained in products in either fixed or free form. It is anticipated that fixed form ENPs will have a low potential to be released to the environment. Applications that contain free ENPs and which therefore pose the greatest risk for environmental exposure include cosmetics and personal care products, paints and coatings, catalysts and lubricants, water treatment products, food and food packaging, human and veterinary medicines and plant protection products.
4. The environmental compartments that are exposed will vary according to the product type (Table 3.3.)
5. Limited information is available on the amounts of ENP-containing products in use and the concentrations of ENPs within these products. This is a major data gap that will need filling before the current and future environmental exposure can be established with any degree of accuracy.

Table 3.2 Available data on concentrations of engineered nanoparticles in different product types

Product type	Engineered nanoparticle	Concentration (%)	Notes
cosmetics and personal care products			
Anti-inflammatory cream	fullerene clusters*	0.05	US Patent 20050136079
laundry detergents	latex$^\$$	0.5 – 10	
eyeliner	fullerene C_{60}, C_{70} & C_{84}*	6	US Patent 5612021
foundation	fullerene C_{60}, C_{70} & C_{84}*	0.1	US Patent 5612021
Face powder	fullerene C_{60}, C_{70} & C_{84}*	0.15	US Patent 5612021
lipstick	fullerene C_{60} & C_{70}*	0.3	US Patent 5612021
mascara	fullerene C_{60} & C_{70}*	5	US Patent 5612021
moisturizing vanishing cream	fullerene clusters*	0.05	US Patent 20050136079
perfume	fullerene clusters*	0.25	US Patent 20050136079
shampoo	Ag$^\$$	0.001 – 0.002	Nanogist Co. (2007)
Skin creams	fullerene $C_{60}$$^\$$	0.25	US Patent 20050136079
soap	Ag$^\$$	0.001 – 0.002	Nanogist Co. (2007)
sunscreen	$TiO_2$$^\$$	5	Oxonica (2007)
	ZnO$^\$$	15.5	Key Skin Care (2007)
toothpaste	hydroxyapatite$^\$$	15	BlanX (2007)
	Ag$^\$$	0.001 – 0.002	Nanogist Co (2007)
paints and coatings			
paints	$Al_2O_3$$^\$$	0.5 - 5	BYK-Chemie (2007)

* - product not thought to currently be in use in the UK; $^\$$- data indicates that products are available in the UK

Product type	Engineered nanoparticle	Concentration (%)	Notes
	SiO_2[$]	15	Laromer PO 9026V
	TiO_2[$]	5	Solacor
	ZnO[$]	7-10	Degussa
scratch resistant coatings	organo-silica*	10	
scratch resistant wood coatings	ZnO*	2	
	CeO_2*	1	
biocidal coatings for construction materials	Ag*	0.001 – 0.1	US Patent 20060272542
Food packaging			
nanocomposites	nano-clay[$]	5	
Water treatment			
remediation of groundwater	Fe*	11.2 kg m^2	
Nano-medicines			
wound dressings	Ag[$]	5	Smith and Nephew (2007)
active ingredients	paclitaxel[$]	1-20	
fungal treatments	amphotericin[$]	100	Daily dosage 5 mg/kg (Albelcet (2007)
cancer treatments	liposomal cytarabine[$]	100	50 mg dose every 14 d for 3 doses (SkyePharma, 2007)
macular degeneration	liposomal verteporfin[$]	100	Single 15 mg dose (Novartis, 2007)
febrile neutopenia	PEG-G-CSF[$]	100	Single 6 mg dose (Amgen, 2007)
acromegaly	PEG-HGH[$]	100	Daily dose of 10 mg (Pfizer, 2007)
Fabric coatings			
Antimicrobial fabric coatings	Ag*	0.005	Lee *et al.*, 2003
Fuel catalysts			
diesel additives	CeO_2[$]	0.001	

* - product not thought to currently be in use in the UK; [$]- data indicates that products are available in the UK

Table 3.3. Major emission routes for different classes of products

Sector/ Application	Nanomaterial Type	Likely Exposure Routes					
		Air	Drinking water	Surface water	Ground water	Wastewater	Soil- waste disposal
Cosmetics and personal care products	TiO_2, ZnO, fullerene (C_{60}), Fe_2O_3, Ag	√	?	√	?	√	√
Catalysts, lubricants and fuel additives	CeO_2, Pt, MoS_3	√		√	?	√	√
Paints and coatings	TiO_2, SiO_2, Ag, quantum dots	√		√	?	√	√
Water treatment & environmental remediation	Fe, Fe-Pd, polyurethane		√	√	√	√	√
Agrochemicals	SiO_2 (porous) as a carrier	√	√	√	?		√
Food packaging	Ag, nanoclay, TiO_2,						√
Pharmaceuticals and medicines	Nanomedicines and carriers	√			?	√	√

4. Fate and behaviour of engineered nanoparticles in the environment

The nature of the exposure of the environment to ENPs will be determined by a range of fate and transport processes occurring in treatment systems, the water and soil environment and in air. This Chapter provides an overview of the data that area available for each of these areas.

4.1. Fate of engineered nanoparticles in wastewater treatment

The principle function of wastewater treatment is to remove solid, organic and microbiological components that cause unacceptable levels of pollution to the receiving body. All wastewater treatment facilities have compliance standards to meet in relation to biological oxygen demand (BOD) and suspended solids. Additional consideration is given to ammonia, nitrate, phosphorus and metals depending on the size of the treatment facilities and the nature of the discharge. Typical wastewater treatment works are thus designed with these components in mind resulting in up to 5 stages of treatment (Table 4.1).

Table 4.1: description of key removal components

Treatment level	Description of removed components
Preliminary	Large solids such as rags, sticks and floatable objects as well as fats oils and greases
Primary	Large suspended solids ad aggregated components
Secondary	Biodegradable organic matter and associated components
Tertiary	Residual suspended solids and colloids
Advanced	Dissolved and colloidal components

The processes most commonly encountered in wastewater treatment include: (1) screens, (2) coarse solids reduction, (3) grit removal, (4) sedimentation, (5) biological treatment and (6) filtration. The majority of the processes work through the application of a physical force and are collectively known as physical processes. The other processes operate through a biological reaction coupled to an adsorption step whereby active microorganisms biologically utilise components as part of their growth cycle and convert dissolved organic components to solids for removal in downstream physical processes.

Extensive searches of available literature databases have confirmed a genuine paucity of information directly related to the fate of nano particles in wastewater. As such the following section considers the potential for removal and the likely key control parameters at each stage of a typical wastewater treatment works. To illustrate the issues, where possible, data is drawn from comparable fields associated with metals and viruses, which occur in a similar size, range to some of the potential nano particles and so offer some insight to fate. However, it must be stressed that firm conclusions are difficult as the association of nano particles within the matrix is

likely to be a controlling parameter and this does not necessarily correlate between nano particles, metals and viruses. As such the data provided is intended as an illustration rather than direct evidence.

4.1.1. Preliminary and primary treatment

The initial stages of wastewater treatment include screens; grit removal; fats, oils and greases (FOG) removal and primary sedimentation. All these processes are intended to remove relatively coarse solids and work in relation to a combination of the size and density of the solids they remove. Screens are simple sieve devices that retain material bigger than the size of the opening. Typical opening sizes are down to 2 mm with most screens being larger than that. Grit or FOG removal and sedimentation work by separating particles based on differential settling characteristics such that in relatively quiescent water flows the large, dense particles will settle out. Consequently, the removal efficiency of nano particles in preliminary and primary treatment processes will depend on the nature of their association in the wastewater matrix. In particular the nano particle will need to be present in the form of a settleable or potentially settleable form. Such association can occur through either association to appropriately size particles within the wastewater or aggregation of nano particles by chelation and complexation with soluble components in the wastewater.

Sedimentation occurs through three mechanisms depending on the solids concentration entering the process: discrete, flocculent and hindered settling. Discrete settling describes an unhindered process driven by gravity and is reasonably well described by a modified form of Stoke's law which takes into account the fractal nature of solid aggregates (Gregory, 2006). Particles with a settling rate (v_p) in excess of the water velocity (v_c) will be removed whilst those with a velocity less than the water flow will be removed proportionally to the ratio of the two velocities:

$$X = \frac{v_p}{v_c} \qquad \textbf{Equation 4.1.}$$

Design of sedimentation processes is based on a hydraulic overflow rate determined as the volumetric flow rate divided by the cross section area of the tank, which provides an average water velocity. Typically values are between 22 and 30 $m^3.m^{-2}.d^{-1}$ which would be expected to remove 60-70 % of the suspended solids. The specific nature of the settling rates of individual wastewaters is very complex but typical settling rates vary between 12 and 96 $m^3.m^{-2}.d^{-1}$ (Figure 4.1). Sedimentation of suspended solids is improved for the lowest hydraulic loading rates (Kempton *et al*, 1987) but the influence of hydraulic rate is not consistent for all particle sizes. The removal of particles greater than 35 μm is largely unaffected by hydraulic rate whilst under 30 μm it has a significant impact.
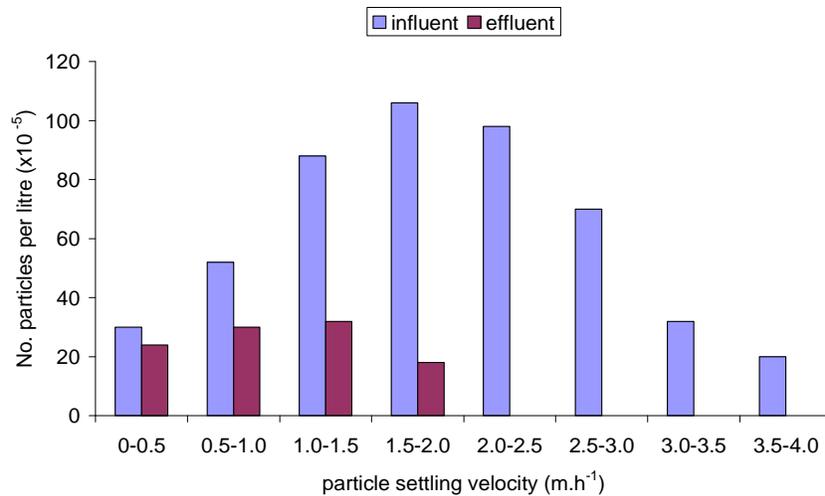
Figure 4.1: distribution of settling velocities across a primary sedimentation tank (adapted from Tchobanoglous *et al*, 2003).

No direct data on the removal of nanoparticles in preliminary or primary treatment has been reported in the literature but comparison to metal systems has shown that between 24 and 56 % removal of metals can occur (Table 4.2). Analysis of the data reveals widely variable numbers from one site to another reflecting likely differences in association. However, in general, metals that are known to occur mainly in the soluble phase, such as Ni, are more poorly removed during sedimentation. Interpretation of the results in terms of nano particles suggest that nano particles that associate with wastewater components that are 35 μm or larger should be well removed. The removal level of nano particles that associate with smaller solids will be dependent on operational variables and those associated with soluble components will be poorly removed.

Table 4.2: Comparable removal efficiency during primary treatment

Metal	Canada	USA	UK	Switzerland	Average
Cd	60	25	-	30	38
Cr	55	36	28	40	40
Cu	33	70	45	40	47
Hg	57	54	-	-	56
Ni	15	-	21	35	24
Pb	66	59	40	50	54
Zn	54	68	41	35	50
Reference	Oliver and Cosgrove, 1974	Barth *et al*, 1965	Brown *et al*, 1973	Roberts *et al*, 1977	

4.1.2. Secondary treatment

The secondary stage of treatment involves an aerobic biological reaction process employing a mixed culture of organisms to oxidise the biodegradable components in

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the wastewater. The culture of organisms exists in either freely suspended flocs (activated sludge, sequenced batch reactor etc.) or in a biofilm (trickling filter, rotating biological contactor etc.). In the reactor large populations of micro-organisms convert the wastewater pollutants into carbon dioxide, water and cellular material. Any substance which is adsorbed or absorbed by the floc or biofilm is removed when the solids are separated in a downstream sedimentation process. Whilst biofilm processes are less well understood it is not unreasonable to assume that the uptake of nano particles by a biofilm will be similar to that of a suspended floc.

Potential mechanisms for removal of nano particles in biological processes are likely to be either: settlement of aggregated particles or adsorption onto the floc or biofilm. The additional removal by settlement over that in the primary tank is due to the improved overall efficiency of secondary sedimentation. Lester (1987) suggests four potential mechanisms of removal of metals in activated sludge all of which are potential routes for nano particle removal:

- physical entrapment of insoluble particles into the floc
- active cellular uptake
- binding to extra cellular polymers
- volatilisation

In the case of metals the removal of insoluble components has been found to be the predominant mechanism for many species (Lester, 1987) although binding to extracellular polymers (EPS) is thought to be an important mechanism for many of the species (Spath *et al*, 1998). EPS are naturally produced by micro organisms and are found either bound to the bacterial cells or detached and in the liquid phase. EPS are known to be a very good complexing agent in either form. The fate of nano particles will depend on which form they bind to: ENPs that bind to EPS associated with biomass solids will be removed during sedimentation whilst ENPs associated with soluble EPS will be stabilised and poorly removed. The bound material will then be removed during sedimentation whereas the loose material will stabilise the nano particles and reduce removal potential.

It is likely that nano particle removal will mirror overall removal of organics in the process due to the binding potential. This is typically controlled in one of two ways. Increasing the ratio of returned activated sludge will effectively dilute the feed and reduce the amount of food available for growth. Alternatively the bacteria are only able to grow at the same rate as they are being lost through sludge wastage such that the sludge age, as controlled by the wastage rate, of the system will have a significant influence over removal levels. Consequently, it is expected that nano particle removal should be enhanced with sludge age. Comparison to previous work on the treatment of metals suggests that removal levels around 40-50% are possible although a great deal of variation is likely (Table 4.3). Extending sludge ages from 6 to 20 days has been shown to increase metal removal by 10-20% (Lester, 1987). Once again metals which predominately remain in the soluble phase are poorly removed and therefore a similar result would be expected for nano particles.

The situation in biological treatment is complicated as the system is living and responds to change. In particular the toxicity of any component introduced into the system has the potential to impact on the performance significantly. The success of

the process relies on a mixed culture of a wide range of organisms to provide a large species diversity. Shifts in diversity will affect treatment efficiency through either EPS release or changes in the formation of flocs reducing downstream sedimentation efficiency. Experience with metals suggests this is most acute when the components enter the system periodically such that the biological system cannot acclimatise to the toxic components. The situation with respect to biofilm processes is likely to be similar as the same mechanism will operate. The major difference is in respect of mixing such that it is possible for nano particles to not contact the biofilm and hence not be removed. Consequently, trickling filters are likely to present a higher risk of not removing nano particles.

Table 4.3: Comparable removal efficiency during secondary treatment

Metal	Canada	USA	UK	Switzerland	Average
Cd	50	63	47	7	41
Cr	54	33	82	50	55
Cu	60	79	77	25	55
Hg	2	-	72	-	68
Ni	1	61	41	15	28
Pb	79	73	53	30	58
Zn	50	78	59	38	58
Reference	Oliver and Cosgrove, 1974	Barth *et al*, 1965	Brown *et al*, 1973	Roberts *et al*, 1977	

4.1.3. Tertiary treatment

Tertiary treatment refers to treatment of secondary effluent to further reduce suspended solids, BOD and ammonia. Process options include deep bed filtration, micro screens, wetlands or advanced sedimentation of which deep bed filtration is the most widely adopted. Deep bed filtration involves the flow of effluent through a bed of media, typically sand, at a relatively slow rate (c 10 $m^3.h^{-1}$). As the water travels through the bed particles are retained by the media. Models to describe filtration have been around for decades based on a combined mechanism of transport and attachment. The former is based on the flow pattern and largely relates to the bed properties whilst the latter depends on the surface properties of both media and pollutant particles. Modern refinements of the models have attempted to combine both processes. Common to all the models is a prediction that the minimum removal will occur for particles of around 700 nm (Figure 4.2) and those below 100 nm should be effectively removed as the Brownian motion of the ENPs will be sufficient to ensure a high collision efficiency with the filter media grains. Ben Aim *et al* (1997) experimentally demonstrated this to a degree by comparing the removal of 460, 870 and 3000 nm diameter latex spheres in a laboratory scale filter. During the initial stages the 870 nm particles were removed to a significantly less extent compared to the others. However, once the filter bed had ripened the smallest particles became the poorest removed. Ripening in such cases refers to the pore spaces in the top layers of the bed being reduced during the initial removal of particles. In normally circumstances removal is expected to improve once the bed has ripened but importantly the work of Ben Aim *et al* (1997) suggests that

this may not be the case for ENPs. No explanation was provided but it is likely to be due to the flow pathways in the bed straightening and so reducing the likelihood of particle media collisions. Surface interactions become very important with respect to filtration of nano particles as retention will depend on the balance of attachment forces holding the particle to the media and Brownian motion driving the particle back into solution.
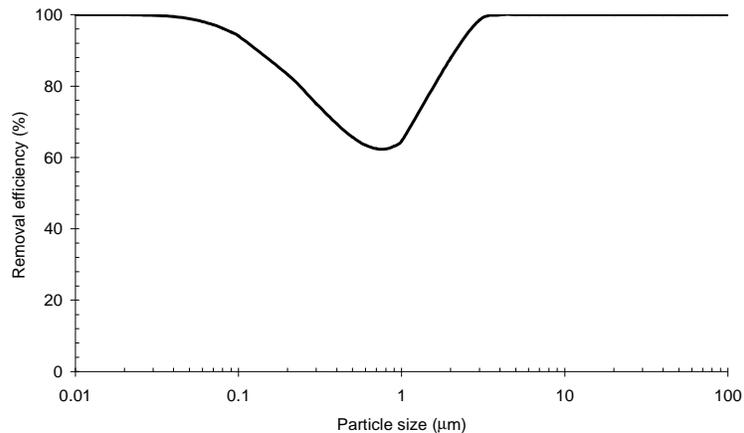

Figure 4.2: theoretical prediction of removal in deep bed filtration

4.1.4. Advanced treatment

Advanced treatment is rarely practiced currently but involves the use of advanced technologies to remove pollutants down to very low levels and target specific types of compounds such as endocrine disrupting chemicals (EDC), metals and viruses. The most relevant option for removal of ENPs is membrane processes. Membrane processes can be viewed as a sub set of screens where the gap sizes are very small. As with screens, membranes will retain all particles bigger than the size of the pore. The reality is more complicated as the structure of the membrane is not particularly simple but removal of particles down to sizes of a few nanometres is possible. The most relevant application of membranes in wastewater treatment relates to the use of membrane bioreactors (MBRs) which represent an alternative secondary biological process whereby the sedimentation tank is replaced by a membrane. Effluent quality from such processes is extremely good such that the technology is most commonly used in cases of water reuse or for coastal discharges where coliform reduction is required. Current uptake of the technology is in excess of 2259 plants worldwide although uptake in the UK is more limited and is mainly focussed in the South West of the country. Typical pore sizes of commercial MBRs are between 40 and 400 nm although during operation a gel layer forms on the membrane reducing the effective pore size to much lower sizes (Table 4.4). Consequently reasonable nano particle removal should be expected from all versions of the technology.

Table 4.4: example pore sizes of commercial MBRs (adapted from Judd, 2006)

Supplier	Pore size (nm)
Colloids engineering systems	40
Huber Technology	38
Kubota	400
Toray industries	80
Siemens Water technologies	40
Zenon	40

Membrane processes provide an absolute barrier to the particles they retain and as such when performance deteriorates it is normally in relation to the throughput rather than the water quality. This occurs as the retained materials accumulate on the membrane surface reducing its permeability in a process commonly called fouling. Theoretical prediction of performance indicates that the maximum fouling and hence performance deterioration occurs with particles within the range 100-400 nm (Sanchis, 2003). However, operational practice has not been able to confirm this and operation of plant without serious fouling is routine when properly

4.2. Fate and behaviour of engineered nanoparticles in water bodies

Once a nanoparticle is introduced into the water environment, there are many processes that will affect their fate, including partitioning to sediment and suspended particulate material, biological degradation (aerobic and anaerobic), and abiotic degradation (including photolysis and hydrolysis). A number of studies have investigated the fate and transport of engineered nanoparticles in water systems. Most of this work has focused on the aggregation behaviour of the particles.

Available data indicate that, following release to water, nanoparticles (including carbon nanotubes, nanoscale zerovalent iron, titanium dioxide and fullerenes) will aggregate to some degree (e.g. Forstner *et al.*, 2005; Phenrat *et al.*, 2007; Dunphy *et al.*, 2006). Aggregates may then settle out (Brant *et al.*, 2005). The degree of aggregation and the size range of the aggregates is dependent on the characteristics of the particle (i.e. type, size, surface properties and, for magnetic metal particles, the intrinsic magnetic moment) and the characteristics of the environmental system (including pH, ionic strength and dissolved organic carbon content)(Hyung *et al.*, 2007; Phenrat *et al.*, 2007; Dunphy *et al.*, 2006). Aggregation reduces the specific surface area of the particles and the interfacial free energy and will therefore reduce particle reactivity. A number of modelling approaches have been proposed for predicting aggregation behaviour in environmental systems (Mackay *et al.*, 2006), however these have yet to be fully evaluated. In the following paragraphs we provide an overview of data the fate of a range of nanoparticle types in water systems.

Fullerenes - under a variety of conditions C_{60} particles form stable aggregates (25-500 nm)(Fortner *et al.*, 2005) with a mean of 75 nm (Lyon *et al.*, 2006). Once an aggregate forms the hydrophobicity and reactivity is considerably changed and the n-C_{60} forms negatively charged crystalline colloids. The aggregate formation process is affected by a range of variables including nanoparticle concentration, formation kinetics and water chemistry. For example, at ionic strengths of 0.05 or less, these

aggregates of n-C_{60} were found to be stable in size (~100 nm) for over 15 weeks although at higher ionic strengths (0.1; as seen in seawater or brackish waters), the aggregates were shown not to remain in solution. The presence of synthetic (e.g. Triton X-100) and natural (e.g. humic substances) surfactants increases the solubility of C_{60} particles in waters (Terashima and Nagao, 2007). Recent data indicate that humic substances, which are naturally present in water bodies, can increase the water solubility of C_{60} 8 – 540 times that in a blank solution (Terashima and Nagao, 2007). HSs also decrease the rate of aggregation (Chen and Elimelech, 2007).

Derivatized fullerenes (i.e. hydroxylated C60 (fullerols) - On addition to water, these particles form clusters with a mean size of 100 nm. The size evolution is dynamic and sensitive to changes in pH and temperature (Brant *et al.*, 2007). The addition of tannic acid, as a surrogate for natural organic matter, had no significant effect on the behaviour of the fullerol particles.

Zerovalent iron – These nanoparticles tend to agglomerate and grow to the micron scale or larger thereby rapidly losing their mobility and chemical reactivity (Mondal *et al.*, 2004; Schrick *et al.*, 2004; He and Zhao, 2005). The aggregates then assemble themselves into a fractal, chain like structure which rapidly sediment out from solution (Phenrat *et al.*, 2007)

Carbon nanotubes – Are extremely hydrophobic and subject to aggregation as they are subject to high Van der Waals interaction forces along the length axis and are thus not readily dispersed (Hyung *et al.*, 2007). Dispersion can be achieved through the addition of surfactants and polymers to the nanotubes. The presence of natural organic matter in solution also has a stabilising effect on the nanotube dispersions (Hyung *et al.*, 2007). The dispersal of carbon nanotubes in natural water bodies may therefore be higher than previously expected. The behaviour of carbon nanotubes has also been shown to be modified in the presence of biota (Roberts *et al.*, 2007). Studies into the interactions of lysophophatidylcholine coated SWCNTs with Dapnnids demonstrated that the invertebrates altered the solubility of the nanotube, probably as a result of the digestion of the lipid coating (Roberts *et al.*, 2007).

Titanium dioxide – When 66 nm particles are applied to water, the particles aggregate to particles ranging in size from 175 – 810 nm (mean 330 nm) (Adams *et al.*, 2006).

Titanate nanotubes (7-10 nm x several hundred nm) – in pure water or under basic conditions, these particles are stable but under acidic conditions they convert to rutile nanoparticles of ca 3nm in size. (Bavykin *et al.*, 2006)

Silicon dioxide – When 14 nm particles are applied to water, the particles aggregate to particles ranging in size from 135 – 510 nm (mean 205 nm) (Adams *et al.*, 2006).

Zinc oxide – When 67 nm particles are applied to water, the particles aggregate to particles ranging in size from 420 – 640 nm (mean 480 nm) (Adams *et al.*, 2006).

Stabilisers may be used in the manufacturing process to reduce agglomeration and enhance the dispersion of engineered nanoparticles. The stabilisers work via either a) electrostatic repulsion where a charged stabiliser is adsorbed to the particle increasing repulsion between particles; or b) steric hindrance where a bulky stabiliser

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is used to impede particle attraction. A wide range of stabilisers has been found to be effective, including thiols, carboxylic acids, surfactants and polymers. The stabilisers not only affect the behaviour of the nanoparticle within a product but can also enhance the mobility of ENPs in the environment (e.g. Tungittiplakorn *et al.*, 2004).

Data on the sorption behaviour of free and aggregated engineered nanoparticles to suspended solids and sediment is lacking from the literature although some studies suggest that, following aggregation selected particles may sediment out and hence it is likely that they will associate with bed sediments. Information on the persistence of engineered nanoparticles in environmental systems is also not available although some polymer based particles (including poly(lactic-co-glycolic acid); gantrez; HSAM; and polypyrrole/poly(D,L-lactide) are known to be degradable in other biological systems and are therefore might be expected to be degraded in the natural environment (Wang *et al.*, 2003; Liu *et al.*, 2006; Dailey *et al.*, 2006; Ochoa *et al.*, 2007).

4.3. Fate and behaviour of engineered nanoparticles in soils

Following release to the soil environment, ENPs may sorb to soil particles, be degraded by biotic and abiotic processes and be transported to water bodies through runoff, leaching and drainflow. Whilst very limited data is available on the interactions of ENPs with soil (e.g. Tungittiplakorn *et al.*, 2004), it is likely that factors affecting fate and transport in the soil environment will be similar to traditional chemicals. Depending on the surface properties of the ENP, adsorbance to soil will likely result from electrostatic attraction, surface bridging, hydrogen bonding or hydrophobic interactions (Ter Laak *et al.*, 2006b). The sorption behaviour is also likely to be influenced by the properties of the soil including pH, organic carbon content, metal oxide content, ionic strength and cationic exchange capacity (e.g. Ter Laak *et al.*, 2006 b, Strock *et al.*, 2005; Sassman and Lee, 2005).

Some experimental data are available on the sorption behaviour of ENPs in soils. For example sorption studies with selected amphiphilic polyurethane nanoparticles demonstrated that these particles are strongly adsorbed to soil particles (polyurethane acrylate anionomers Kd = 0.33-1.49; poly(ethylene glycol)-modified urethane acrylate Kd = 0.69) (Tungittiplakorn *et al.*, 2004).

Environmental transport studies indicate that NPs will exhibit differing mobilities in the soils. Selected NPs have been shown to have the potential to contaminate aquifers (Lecoanet *et al.*, 2004). Mobility in porous media varies depending on nanomaterial type (Lecoanet *et al.*, 2004), for example SWNTs and fullerols appear to pass through porous media more quickly than C60. However these studies were performed using glass beads so the applicability of the results to natural soil systems is unknown. Other studies with ampiphilic polyurethane nanoparticles showed these particles to be mobile through a sandy aquifer material. Environmental conditions such as pH of the surrounding environment may also be very important in determining the degree of transport (e.g. Dunphy Guzman *et al.*, 2006). The fate and mobility of the materials may also be affected by modifications to the ENP such as capping and wrapping of carbon nanotubes with surfactants or the functionalization of C60 (Lecoanet *et al.*, 2004).

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The behaviour of colloidal material in the soil environment has been extensively studied and models have been developed for predicting behaviour (e.g. Grolimund *et al.*, 2001; Dunphy Guzman *et al.*, 2006). Transport in porous media can be described by three mechanisms: interception of the particle by the media; sedimentation due to gravity and diffusion from Brownian motion; and deposition. As engineered nanoparticles may be of similar size to colloids, it is possible that these approaches could be applied to predict the behaviour of ENPs in the soil environment. However the extent to which engineered nanoparticles behave differently to colloids has yet to be established.

4.4. Fate of engineered nanoparticles in the air environment

Aitken *et al* (2004) discuss the mechanisms of diffusion, agglomeration, and deposition for nanoparticle aerosols, and the possible resuspension of aerosol from deposited nanoparticles. We do not reproduce the full detail of that discussion but summarise the key points that are important for assessing exposure to airborne nanoparticles.

Particle diffusion (Brownian motion) occurs because particles are bombarded by molecules of gas, and when particles are very small the discrete impact of individual gas molecules imparts a velocity to the particle and successive impacts produce changes in the direction of the acquired velocity thus producing a random motion. As particle size decreases towards the molecular size, their diffusion behaviour becomes closer to that of a vapour.

Near the source of release, particle concentrations may be very high so that agglomeration of particles is likely to occur due to Brownian diffusion. Maynard (2005) adapted a graph (from Hinds (1999)) to show the change of number concentration of aerosols as a function of time. With concentrations of the order of 10^{10} particles per cm^3, the particle concentration is declining significantly within 10 seconds, whereas at a concentration of 10^6 particles per cm^3, the concentration is changing over hours. The graph was produced for particles with a coagulation coefficient $K=5\times10^{-6}$ m^3/s, which corresponds to a particle diameter of about 200 nm (see Appendix A11(a) of Hinds for values of K tabulated for a range of particle diameters). At 10^6 particles per cm^3, the mass concentration (for spherical particles of unit density) would be about 0.8 ng/m^3. At 10^{10} particles per cm^3, the mass concentration would be about 8 mg/cm^3.

Table 4.5. Coagulation half life for mono-disperse nanoparticle aerosol at concentrations ranging from 1 g/m^3 to 1 ng/m^3, for material of density 1000 kg.m^{-3}, for particles with diameters in the range 1 to 20 nm.

Particle diameter	Particle number	1 g/m3	1 mg/m3	1 µg/m3	1 ng/m3
nm	for 1 g/m³	ms	s	minutes	hours
1	1.9 ×10²¹	0.0022	0.0022	0.04	0.61
2	2.4 ×10²⁰	0.012	0.0120	0.20	3.33
5	2.4 ×10²⁰	0.12	0.12	2.00	33.33
10	1.9 ×10¹⁸	0.7	0.70	11.67	194.44
20	2.4 ×10¹⁷	3.8	3.80	63.33	1055.56

Table 4.5 above, for particles with diameter of 20 nm or less, shows the rate of coagulation expressed as a half life, for a wide range of particle concentrations. This table illustrates that a 1000 fold decrease in particle concentration produces a 1000 fold increase in the half life for coagulation. (Note that the units for time increase from ms to s to minutes to hours from left to right across the table).

The values of the coagulation coefficients used by Hinds and by Preining (the source of Table 4.4.) are of similar but not identical magnitude for given particle size. For example, for a particle diameter of 20 nm, Hinds gives $K = 11.5 \times 10^{-16}$ m^3/s whereas Preining gives $K = 15.1 \times 10^{-16}$ m^3/s. The difference may arise from different choices regarding conditions such as temperature (the temperature being stated by Hinds but not by Preining). However, for the purpose of this report the values are sufficiently similar to indicate the significance of agglomeration.

For polydisperse aerosols, the rate of coagulation is expected to be greater than for mono-disperse aerosols. Small rapidly diffusing particles are likely to collide with larger slower-moving particles, see for example Hinds (1999). Hinds summarises the influence of agglomeration on the particle size distribution of atmospheric aerosols. There is a tri modal distribution, with the smallest particles (mode about 20 nm) being known as the *nuclei mode,* the largest particles (mode about 10 µm) as the *coarse particle mode ,* and the particles of intermediate size *(*mode about 0.5 µm) as the *accumulation mode.* The accumulation mode, as suggested by the name, tends to accumulate because removal mechanisms are weak for this size range of particles. The accumulation mode contains nanoparticles / nano materials that have agglomerated with other particles.

Some of the more detailed models of dispersion address mechanisms of particle deposition and rain-wash out, and both of those mechanisms are particle size dependant. Changes in particle size are obviously relevant to those mechanisms. We discuss those models later.

5. Modelling exposure to engineered nanoparticles

It is clear from the previous sections that our understanding of the current usage environmental fate of ENPs is limited and that very little data are available on amounts of ENPs in use and on the environmental properties of these in wastewater, surface water, soil and the air environment. Therefore in this section we describe a series of algorithms for estimating potential environmental exposure of ENPs based on the data available. The algorithms are then applied to predict concentrations of ENPs in air, soil and water arising from a range of the applications described in Chapter 3.

5.1. Prediction of exposure concentrations in water bodies

The main routes of entry of ENPs to water will be from either: 1) the direct entry of ENPs to waterbodies from bioremediation; 2) Inputs from spray drift following use of agrochemicals; 3) Runoff from contaminated soils; 4) Aerial deposition; and 5) Emissions from wastewater treatment plants. In the following sections we present a series of simple algorithms and scenarios for estimating concentrations of ENPs in water bodies from these different routes.

5.1.1. Direct application to water bodies

A conservative estimation of concentration of an ENP arising from direct application to water bodies (e.g. for bioremediation purposes) can be obtained using a simple dilution equation (Equation 1). The water body dimensions used are determined by the nature of the receiving water body.

$$PECsw = \frac{A}{W * D * L * 1000}$$
Equation 5.1

Where:

PECsw = predicted concentration in surface water (mg l^{-1})
A = application rate of ENP (mg)
W = width of the water body (m)
D = depth of the water body (m)
L = length of the water body (m)

5.1.2. Inputs from soil systems

ENPs may be released to soils for remediation purposes, as a result of pesticide application, from veterinary usage or as a result of the application of sewage sludge to land as a fertiliser. The ENPs may enter water bodies during the application process (e.g. spray drift of pesticides) or through runoff, drainage and leaching. The exposure of surface waters resulting from these different input routes can be

estimated using a simple model proposed by the Forum for Co-ordination of Pesticide Fate Models and their Use (FOCUS, 2001).

The model (Equation 5.2) considers inputs from spray drift and runoff. For pesticides, the amount entering from each of these routes is determined by the nature of the land to which the ENP is applied and the distance of a stream from an application area and default input values are available (Table 5.1). For other input routes, inputs from spray drift are unlikely to occur so runoff inputs only are considered (it is assumed that 10% of the applied dose enters the surface water via runoff). The algorithm assumes that a 1 ha field is linked to a 3×10^5 litre stream (Table 5.2).

$$PECsw = \frac{A(SD) + A(R)}{W * D * L * 1000} \quad \textbf{Equation 5.2}$$

Where:

PECsw = predicted concentration in surface water (mg l^{-1})
A = application rate (mg/ha)
SD = fraction released in spray drift (from Table 5.1)
R = fraction of applied ENP entering via runoff (from Table 5.1)
W = width of the water body (m)
D = depth of the water body (m)
L = length of the water body (m)

5.1.3. Inputs to water bodies via the sewage system

Many ENP containing products (including pharmaceuticals, cosmetics and personal care products and paints and coatings) will be released to aquatic systems via the sewage system. For these ENPs, a conservative estimate of concentrations in receiving waters can be obtained using an adaptation of the surface water exposure algorithm developed by the Committee for Medicinal Products for Human Use (CHMP, 2006). This algorithm (Equation 5.3) estimates surface water concentrations based on the concentration of ENP in a product and the amount of product used per capita per day. It assumes that the usage of a product is even over the year and that the sewage system is the main route of entry. Default values for use in the algorithm are given in Table 5.3. Typical usage data for a range of product types is given in Table 5.4. In instances where data are available on removal of an ENP in a sewage treatment system, this can be used to refine the exposure estimates.

Table 5.1 Spray drift and runoff inputs into surface water from fields of different characteristics

Crop	Distance crop-water (m)	Drift (% of application)	Runoff/drainage (% of application)
cereals, spring	1	2.8	10
cereals, winter	1	2.8	10
citrus	3	15.7	10
cotton	1	2.8	10
field beans	1	2.8	10
grass / alfalfa	1	2.8	10
hops	3	19.3	10
legumes	1	2.8	10
maize	1	2.8	10
oil seed rape, spring	1	2.8	10
oil seed rape, winter	1	2.8	10
olives	3	15.7	10
pome / stone fruit, early applications	3	29.2	10
pome / stone fruit, late applications	3	15.7	10
potatoes	1	2.8	10
soybeans	1	2.8	10
sugar beet	1	2.8	10
sunflower	1	2.8	10
tobacco	1	2.8	10
vegetables, bulb	1	2.8	10
vegetables, fruiting	1	2.8	10
vegetables, leafy	1	2.8	10
vegetables, root	1	2.8	10
vines, early applications	3	2.7	10
vines, late applications	3	8.0	10
application, aerial	3	33.2	10
application, hand (crop < 50 cm)	1	2.8	10
application, hand (crop > 50 cm)	3	8.0	10
no drift (incorporation or seed treatment)	1	0	10

Table 5.2 Surface water definitions

Parameter:	value
water depth (cm):	30
sediment depth (cm):	5
effective sediment depth for sorption (cm):	1
sediment oc (%):	5
sediment bulk density (kg/L):	0.8
ratio of field to water body:	10

$$PEC_{sw} = \frac{C_{ENP}.U_{prod}.(1 - R_{stp}).F_{pen}}{WW_{inhab}.D}$$

Equation 5.3

Where:

PECsw = predicted concentration in surface water (mg l^{-1})
C_{ENP} = concentration of engineered nanoparticle in product (mg g^{-1})
U_{prod} = daily usage of product (g capita^{-1} d^{-1})
R_{stp} = fraction of ENP removed during sewage treatment
F_{pen} = market penetration of nano product
WW_{inhab} = amount of wastewater produced (l capita^{-1} d^{-1})
D is the dilution factor in the receiving water

5.2. Prediction of environmental exposure concentrations in soils

The main routes of exposure of engineered nanoparticles in soils will be: 1) through the application of remediation technologies; 2) the application of plant protection products; 3) the excretion of nanomedicines used in veterinary products; 4) aerial deposition and 5) the application of sewage sludge as a fertiliser. In the following sections we present a series of simple algorithms and scenarios for estimating concentrations of ENPs in water bodies from these different routes.

5.2.1. Direct application to soils

For ENPs that are applied directly to soils, a 'worst' case estimation of the concentration in soil can be estimated using the simple dilution model given in Equation 5.4.

$$PEC_{soil} = \frac{A}{D_{soil}.RHO_{soil}}$$

Equation 5.4

PEC$_{soil}$ = concentration of ENP in soil (mg kg^{-1})
A = application rate of the ENP (kg m^2 yr)
D$_{soil}$ = soil mixing depth (m)
RHO$_{soil}$ = soil bulk density (kg m^3)

5.2.2. Prediction of concentrations in soils resulting from application of sewage sludge to land

For products that are released to sewage treatment systems, it is possible that the ENPs in these products will associate with sludge particles within the treatment system. The sludge is ultimately removed from the treatment system and may then be applied as a fertiliser to land providing a route by which ENPs in consumer products can reach the soil environment. In order to predict the concentrations of

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ENPs in soil arising from this route, it is first necessary to estimate the concentration of the ENP in the sludge. This can be estimated, using Equation 5.5, from the concentration of the ENP in a product, the usage characteristics of the product and the sludge production rate per person per day. The concentration in soil is then calculated based on sludge application rates and the concentration in sludge, using equation 5.6. Default values for use in these algorithms are given in Table 5.3. In instances where data are not available on removal in sewage treatment, a worst-case concentration in sludge and soil can be obtained by assuming all of the ENP released adsorbs to sludge (i.e. $R_{stp} = 1$)

$$PEC_{sludge} = \frac{C_{ENP}.U_{prod}.R_{stp}.F_{pen}}{S_{inhab}}$$ **Equation 5.5**

Where:

PEC_{sludge} = predicted concentration of ENP in sludge (mg kg^{-1})
S_{inhab} = sludge production (kg capita^{-1} d^{-1})

$$PEC_{soil} = \frac{PEC_{sludge}.A_{sludge}}{D_{soil}.RHO_{soil}}$$ **Equation 5.6**

Where:

PEC_{soil} = concentration of ENP in soil (mg kg^{-1})
A_{sludge} = sludge application rate (kg m^2 yr)
D_{soil} = soil mixing depth (m)
RHO_{soil} = soil bulk density (kg m^3)

Table 5.3. Default values for exposure assessment for ENPs entering the environment via the sewer system

Parameter	Value	Reference
WW$_{inhab}$	200	CHMP (2006)
F$_{pen}$	0.1, 0.5, 1.0	-
S$_{inhab}$	0.07	Mogoarou (2000)
A$_{sludge}$	0.5	EU (2003)
D	10	CHMP (2006)
D$_{soil}$	0.2	EU (2003)
RHO$_{soil}$	1700	EU (2003)

Table 5.4. Usage scenarios for emissions to wastewater treatment

Product type	Emission g/pc/d	Notes	Reference
Antiperspirant	0.61	Dose = 0.7 g/d and 86.5% of population use product	Loretz *et al.*, 2005 and 2006
Body lotion	2.20	Dose = 6.0 g/d and 36.6% of population use product	Loretz *et al.*, 2005 and 2006
Body wash	0.32	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Cleaners	0.3	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Deodorants	0.08	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Eyeliner	0.0016	Dose of 0.005 g/g and 32.6% of population use product	SCCNFP, 2003
Face cream	0.94	Dose = 1.6 g/d and 59.1% of population use product	SCCNFP, 2003
General creams	0.77	Dose = 2.4 g/d and 31.9% of population use product	SCCNFP, 2003
Hair conditioners	0.47	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Hair styling products	0.10	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Lime deposit removers	0.11	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Lipstick	0.015	Usage of 0.04 g/d and 37.8% of population use product	SCCNFP, 2003
Paint	0.09 - 0.36 ml/pc/yr	Data on usage in the UK and release of 1-4% during cleaning	British Coatings Federation (2007); EU (2003b)
Laundry detergents	10.1 – 20.5	Data for USA, Sweden, Denmark, Finland and Norway	Eriksson *et al.*, 2002
Mascara	0.0082	Dose of 0.025 g/d and 32.6% of population use product	SCCNFP, 2003
Oral hygiene products	0.7	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Perfume	0.22	Dose = 0.5 g/d and 44.4% of population use product	Loretz *et al.*, 2005 and 2006

Product type	Emission g/pc/d	Notes	Reference
Shampoo	1.83 – 6.30	Data for Sweden and Denmark	Eriksson *et al.*, 2003 and 2002
Shaving foam	0.07	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Soap	2.5	Data for Sweden	Eriksson *et al.*, 2002
Skin care products	1.3	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003
Softeners	16.4	Date based on use in Europe	Eriksson *et al.*, 2002
Sunscreen	9.81	Dose = 18 g/d and 54.5% of population use product	SCCNFP, 2003
Toothpaste	1.34	Dose = 1.4 g/d and 95.5% of population use product	SCCNFP, 2003
Window cleaners	0.03	Survey of home chemical usage in Denmark	Eriksson *et al.*, 2003

5.3. Prediction of exposure concentrations in air

Three example scenarios are considered for modelling exposure of the air component: 1) exposure of the consumer using personal care products; 2) exposure as the bystander exposed to traffic emission; and exposure within the local area to fugitive emissions from industrial facilities. These three selected examples illustrate many of the issues in modelling aerial exposure.

5.3.1. Exposure from personal hygiene and skin care products

A simple dilution model (Equation 5.7) provides a useful first indication of likely exposure in simple situations. For example, some simple assumptions can indicate the likely exposure of an individual while using personal hygiene products as aerosol sprays. If the hygiene product is sprayed onto the individual's skin in a delivered quantity Q, and a fraction f escapes as aerosol, and the proportion of the nanomaterial in the product is p, then the exposure concentration of nanomaterial to which that individual is exposed may be estimated as:

$$C = \frac{f.Q.p}{V}$$ **Equation 5.7**

where V is the typical volume of air into which the product is mixed by the action of spraying. The cumulative exposure of that consumer might then be derived by making an estimate of the time T that a consumer typically remains in that location after applying the product. If T is a short time (e.g. 10 minutes in the bathroom), then dilution with air change and mixing can be ignored and the product $C.T$ is a reasonable estimate of the typical consumer's exposure. If the consumer or other individuals are likely to remain in that location, then allowance for dilution into the general volume of the room and with the typical air change rate for domestic premises is needed. A study funded by the UK Atmospheric Dispersion Modelling Liaison Committee and available from their website (Milner *et al*, 2004), provides a tabulation of the values used for rate of change of air in various premises. An estimate of the mean typical value for residential premises in northern Europe is 0.4 air changes per hour, with the range being from 0.2 to 1.0. For UK residential premises, mean values have been taken as 0.44 changes per hour during winter, and 0.62 in summer. These are only a few of the values that they quoted, but the others are similar, with a few values being slightly higher. A reasonable precautionary estimate of likely exposure would be to take an air change rate of 0.2 changes per hour. If there are N air changes per hour, then the change per second is k=N/3600. The average room concentration can be expected to diminish exponentially at that rate. If the personal hygiene product has been used in a relatively small room such as a domestic bathroom, then we might assume that the initial concentration C from the equation above is approximately the same as the room average concentration. The cumulative exposure of the consumer per usage (E_u) can be estimated using Equation 5.8.

$$E_u = \int C(t)dt = \int_0^T \frac{f.Q.p}{V} e^{-kt} dt$$ **Equation 5.8**

The integration is from time t=0 (when the product is used) to a time T when the consumer leaves the room where the product was used.

5.3.2. Modelling framework for exposure to nanoparticles from traffic

A simple modelling approach

In an urban street, exposure occurs in the proximity of the source and consequently there are relatively short timescales between generation and exposure. Therefore, there is limited scope for condensation or deposition mechanisms to affect the dispersion of particles, especially for very small particles. So dispersion of the fine particulate pollution is likely to be much the same as for gaseous pollutants.

Le Bihan *et al,* (2004) produced real time measurements of particle concentration and gas concentration that allowed them to examine the expected similarity between dispersion of gaseous and particulate pollutants from traffic within an urban street canyon. They found that the expectation was supported and confirmed by their results from two extensive measuring campaigns conducted in a street in Copenhagen, Denmark. They reported that "*The measured particle number concentrations, especially below 100 nm, reveal very similar dependence on the meteorological conditions as the NO$_x$ concentrations. This underpins the conclusion that dilution properties are similar for particles and NO$_x$.*"

For particles greater than 100 nm, they found that the correlation between real time NO$_x$ concentrations and particle concentrations diminished, and correlation became progressively less as concentrations were measured in increasing particle-size intervals from 100 to 700 nm. They concluded that this indicated long range transport of particles greater than 100 nm from other sources of particulate pollution.

Le Bihan *et al* used the Danish Operational Street Pollution Model (OSPM) to calculate a dilution factor F. They stated that the OSPM had been shown (in a previous publication by Berkowciz, (1996)) to give a satisfactory description of the gaseous pollutant dispersion in the urban streets derive an emission rate Q for pollution from traffic in the street. The relationship between concentration C and emission was expressed as:

$$C = Q.F + C_{background}$$ **Equation 5.9**

Rearranging the equation gives an estimate for the emission rate Q:

$$Q = \frac{C - C_{background}}{F}$$ **Equation 5.10**

With concentration expressed in quantity (e.g. particle number) per unit volume, and the emission rate Q in quantity per unit time and per unit length of street, the dilution factor F is in the dimensions of time per unit area. The inverse of F would be a dilution rate, in area per unit time.

The relationship between emission rate and dilution sources also applies to point sources but in that case the dilution rate would be in the units of volume / time.

For emission of engineered nanoparticles, emission may be from a point source (e.g. a stack emission), a line source (road traffic stream with fuel additives), or an area source (fugitive emissions from an industrial site or research buildings).

Dispersion models within spreadsheet tools

The Highways Agency website provides a "Design manual for roads and bridges" which gives guidance (in Volume 11 section 3, Part 1) on the work that local authorities should carry out to assess the impacts of new road schemes on local and regional air quality. The design manual uses a screening method that is available in the form of a spreadsheet tool from the Highways Agency website (http://highways.gov.uk/contracts/index.htm#2 in the DMRB section.

Chapter 2 of Section 3 of the design manual describes how the spreadsheet tool produces estimates of concentrations due to traffic emissions on roads. An equation describing the decrease in pollutant concentration with distance from the road was derived from calculations made using an atmospheric dispersion model developed at the Transport Research Laboratory (*however, no details of that model are given in the manual).* The equation was originally developed to forecast the concentrations of carbon monoxide only, and it is described as having been extensively validated for that purpose. For other pollutants, an assumption is made that their dispersion will be the same as that of carbon monoxide so that their concentrations will be in proportion to their rates of emission. The manual notes that this assumption is likely to be valid for non-reactive gases, including volatile hydrocarbons and total oxides of nitrogen. Exhaust particles, because of their small size, are expected to behave similarly to gases. However, the manual recognises that there may be some inaccuracies for particles because of their agglomeration, deposition, and possible adsorption of atmospheric constituents such as water vapour.

This equation, derived as described, gives the traffic contributed concentration C_{Traf}

$$C_{Traf} = 0.17887 + 0.00024d - \left(\frac{0.295776}{d}\right) + \left(\frac{0.2956}{d^2}\right) - 0.0421 \cdot \ln(d) \textbf{ Equation 5.11}$$

According to this equation, the traffic contribution to pollutant concentration at a given distance from the road is as plotted in Figure 5.1. The concentration is expressed relative to the rate of emission from vehicles.
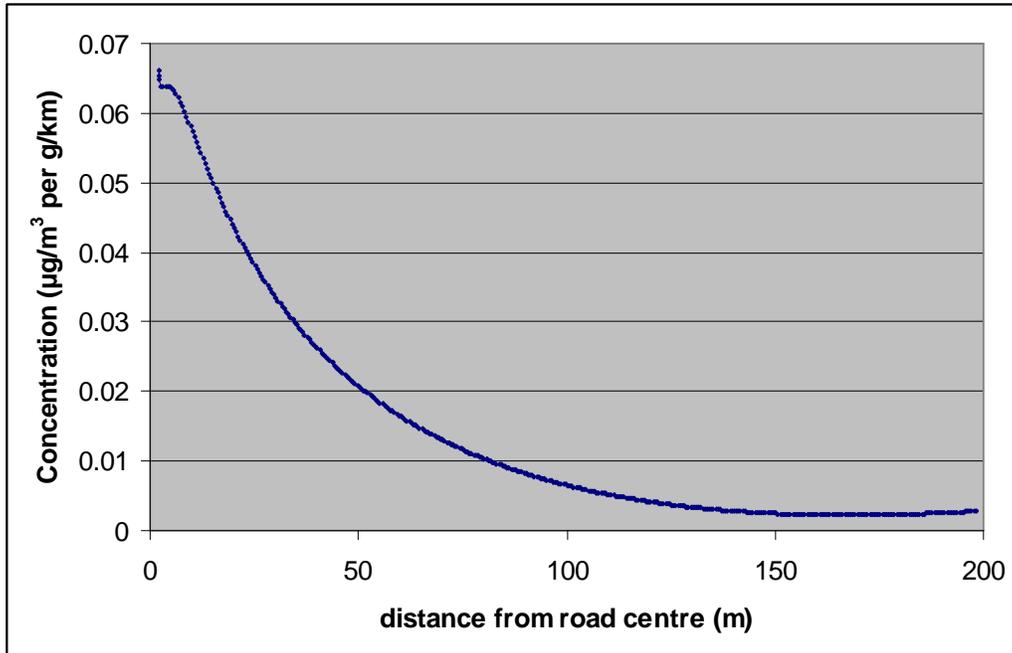
Figure 5.1 Traffic contribution to pollutant concentration as a simple function of distance from the road centre and relative to emission rate (g/km) from vehicles (equivalent to a graph shown in the Design Manual for Roads and Bridges)

The design manual states that the above equation was derived on the assumptions of: a windspeed of 2 m/s; and wind directions being uniformly distributed around the compass. The assumed 2 m/s is believed to be lower than windspeeds typically found in the UK, and therefore the equation tends to over estimate concentrations. The assumption of a uniform distribution of wind directions is convenient but makes no allowance for locally prevailing winds, and therefore may lead to over or underestimates. It would appear likely that the equation above should hold equally well for nanoparticles emitted for traffic as for micron size particles.

Emission factors for using the spreadsheet tools

The National Atmospheric Emissions Inventory (NAEI) provides estimates and projections of the changing composition of the UK fleet of vehicles, and estimates of the emission factors for NO_x and particulates for each category of vehicle http://www.naei.org.uk/other/uk_fleet_composition_projections_v2.xls . These data can be used in the tools provided at http://www.airquality.co.uk/archive/laqm/tools.php?tool=emission.

One of the tools available from this site via a hyperlink (Emissions Factor Toolkits Single Link Version [2e]) provides estimates of the emission per km of road. The data which is fed into the tool is the mix of the vehicle types, and if that is in the simple form of the proportion of light duty vehicles (LDV) and heavy duty vehicles (HDV), road type (urban, rural or motorway), and speed, then the model supplies a standard breakdown of 7 types of vehicle. For example, with LD at 30% and HD at 70%, the mix of traffic is estimated to be as given in Table 5.5. The equation derives emission factors as a function of vehicle type and vehicle speed.

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Table 5.5. Example of a distribution of vehicle mix, typical urban mix (from 1999 NAEI traffic projections, as used in EFT)

Vehicle	% of Vehicle Type
Petrol Cars	71
Diesel Cars	14
Petrol LGV	1
Diesel LGV	10
Rigid HGV	2
Articulated HGV	1

5.3.3. Modelling framework for exposure from industrial stack sources

The Gaussian plume model has been widely used to describe the horizontal and vertical spread of a plume of material. For example, it describes the dispersion of a plume from a stack of height h above the ground. Nano-particles might be emitted from stacks if the stack is the outlet from ventilation in a manufacturing facility (making or using nano-particles) or an incinerator once nano-materials go for waste at the end of the product life cycle.

The model treats the dispersion as being characterised by standard deviations σ_y and σ_z in the horizontal and vertical directions respectively. The basic equation for concentration C at a position defined by rectilinear co-ordinates is:

$$C(x, y, z) = \frac{Q}{2\pi \cdot u_{10} \cdot \sigma_z \cdot \sigma_y} \cdot \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2} + \frac{(z-h)^2}{\sigma_z^2}\right)\right]$$ **Equation 5.12**

where
x = rectilinear coordinate along the wind direction (m),
y = rectilinear coordinate cross wind (m),
z = rectilinear coordinate above ground level (m),
Q = the emission rate (quantity per unit time, #.s^{-1})
u_{10} = wind speed at 10m above ground level (m. s^{-1})
σ_y = standard deviation of the horizontal Gaussian distribution (m)
σ_z = standard deviation of the vertical Gaussian distribution (m)
h = the height of the emission source above ground level (m).

The values of the standard deviations σ_y and σ_z (for the horizontal and vertical distributions) are dependant on the meteorological conditions, the terrain conditions, and the distance from the source. Empirical relationships have been established to estimate suitable values of σ_y and σ_z for a range of typical conditions, as described for example by Clarke (1979). The turbulent dispersion in the atmospheric boundary layer originates from two main sources; there are eddies formed by wind flowing over and round obstacles on the ground, and there is transfer of turbulent energy from high levels of the atmosphere. The transfer of energy from higher layers to lower layers is greatly assisted if there is buoyant convection of warm air rising from

the ground, as happens when the ground is being warmed by the sun. Conversely, if the upper layers are heated by the transverse rays of the evening sun, then there can be a temperature inversion and the upper layers become warmer and more buoyant and that impedes mixing and transfer of energy into the lower boundary layer (Schlicting, 1979).

The atmospheric stability conditions have been described qualitatively as Pasquill Stabilities, labelled A to G. Category D describes neutral conditions, with zero vertical heat flux by convection. These Pasquill categories can be estimated from the degree of cloud cover, and mean surface wind speed (see for example, Clarke 1979).

The Gaussian dispersion equation has also been modified to cope with the situation where the vertical mixing has developed to the stage where the pollutant has reached the upper and/or lower edges of the turbulent boundary layer, and behaves as though it is trapped in that layer being reflected back from the edge of the layer. Again, the adapted equation should apply to nanoparticles as to other particulate pollution, as the particle size dependent velocities (e.g. gravitational settling velocity or diffusion) are negligibly small compared to the velocities driven by turbulence, convection and advection in the atmosphere when considering dispersion in the short and medium range from sources. Short range and medium range have been defined as being from about 100 m to some tens of kilometres (e.g. Clarke, 1979).

However, for dispersion over longer distance, the loss of particles due to deposition needs to be taken into account.

Expected uncertainty in Gaussian plume model predictions

Once modelling is applied in an attempt to estimate likely exposure to nanoparticles, there is likely to be a need to compare model predictions with measurements of actual concentrations to validate the application of the model. Validation of a model in chosen circumstances strengthens its application more widely, and models are likely to be necessary to extrapolate from limited data. Therefore, it is important to recognise the variation that is to be expected in any such comparison.

The factors that contribute to the uncertainty in predictions of concentrations from dispersion models have been mentioned at the outset of discussing exposure by emissions to air (the random nature of atmospheric dispersion, idealisations introduced in modelling the process, estimates of parameters of models, and numerical error from approximations and grid sizes in computational routines). The Gaussian model predicts the dispersion relative to a defined wind direction. These and other factors are discussed by Jones *et al* (1986). They cite data from an American Workshop on the likely range of predicted to observed concentration, and these ranges are shown in Table 5.6. These data show that the average concentration on the centre line of the plume is likely to show a good consistency between observed and predicted, provided that the centre line is accurately located for the observations. However, the stochastic nature of dispersion means that concentrations at specific hour and locations may vary from a tenth to ten fold the predicted level. Long term averages at a specific point are expected to be within a half to twice the predicted value. Monthly and seasonal averages should be between a quarter to fourfold of the predicted value.

Table 5.6. Summary of expected range of predicted to observed concentrations, for validation studies on the Gaussian plume dispersion model

Dispersion modelling and monitoring scenario	Likely range of predicted to observed concentration
Highly instrumented flat terrains; ground-level centre-line concentration within 10 km of a low level source, in steady atmospheric conditions[†]	0.8 – 1.2 [†]
Specific hour and receptor point, flat terrain, steady meteorological conditions, within 10 km of a release	0.1 - 10
Long term average concentrations at a specific point, flat terrain, steady meteorological conditions, within 10 km of the release point.	0.5- 2
Monthly and seasonal averages, flat terrain 10 – 100 km downwind	0.25 -4

[†] The range in the first row has no allowance for errors in locating the centre line of the wind direction. The estimate also assumes a considerable amount of local meteorological data for the site on wind speed and direction e.g. at two heights, and with standard deviations on the horizontal and vertical directions. Jones (1986) commented that without these data, the range would be larger by a factor of 3 or 4.

Some important conclusions follow from these indications of the likely range of predicted to observed concentrations.

1. Without extensive local meteorological data (as indicated in the footnote to the table), the range for the ratio of predicted to observed concentration will be wide. Therefore, any validation (or calibration) of modelled exposure by comparison with observations will need to be tempered by realistic expectations of wide variation. For example, if specific situations relevant to nanoparticles are addressed by a combined use of measured and modelled concentrations to estimate likely exposure, the likely finding of wide ranges in the ratio should not be regarded as a consequence of the properties of nanoparticles. However, if the observations of concentrations have uncertainty arising from the difficulty in measuring the concentrations of nano-particles, then that would add to the overall variation.

2. It is important to draw on the wider body of experience with models to estimate the likely suitability of dispersion models for nano-particles, because comparisons between predicted and observed concentrations need extensive data for robust validation exercises;

3. The ranges in the final two rows of Table 5.6 indicate that predicted average exposure concentrations are a good indication of the approximate actual concentration, at least in reasonably simple circumstances such as flat terrain and stable weather conditions.

The Gaussian models have been extended and adapted to take account of rain washout, deposition of particles, coastal conditions, the dispersion due to wakes of buildings, and continuous release over prolonged time (under changing weather conditions).

Particle size dependent mechanisms

Where the deposition of particles, under dry and/or wet conditions, needs to be taken into account then there are liable to be differences due to particle size. Gravitational sedimentation velocities are proportional to the square of the particle diameter, and proportional to the particle density. So sedimentation rates will be lower for small particles than for larger particles.

Particle size also determines the efficiency of washout of airborne particle by rain. There are two mechanisms involved in washout: inertial capture of dust particles by falling rain drops, and (within a rain cloud) formation of raindrops around particles as condensation nuclei. For particles below the cloud level, the inertial capture is the important mechanism. For submicron particles, motion by Brownian diffusion leads to coagulation which can be quite rapid for high concentrations of particles. So from theoretical calculation of the impaction and diffusion capture, a minimum washout coefficient is expected for particles of about 0.5 µm diameter. The exact diameter would also depend on the rain droplet size, which varies considerably. Due to the diffusion component of capture, the rainfall washout coefficient is likely to be as large or larger for 100 nm size particles as it is for particles of about 5 µm diameter (see for example the data summarised by Clarke, 1979).

5.3.4. Computational Fluid Dynamic (CFD) Models of dispersion

In some situations, it may be appropriate to have the best possible prediction of likely dispersion in the event of a significant emission event (e.g. total failure of containment facilities for the manufacture or storage of industrial quantities of engineered nanoparticles). A detailed model which takes account of local conditions may form the basis for deriving simpler equations (such as that offered in conjunction with Design Manual for Roads and Bridges) which represent likely dispersion in typical circumstances.

Computational Fluid Dynamic models essentially attempt to describe the dispersion by numerical solution of the equations that describe the turbulent flows. Inevitably, any model represents a simplification and an idealisation of the real situation. CFD models came into widespread use for modelling dispersion during the 1990s. They are in principle the best analysis for specific situations, but the simpler models (such as the Gaussian plume model) will remain useful for many applications and may well still be adequate and suitable for many analyses of emissions of nano-particles.

It is important to understand enough of how the models differ in order to be able to assess which models (or models) would be adequate for any specific situation in which there may be exposure to emissions of nanoparticles in air.

Choice of CFD models

In a paper presented at a "Workshop on Reliability of Atmospheric Dispersion Models" held by the NRPB in 2001, Hall summarised the potential importance of differences between the available and widely used CFD (computational fluid dynamics) models of atmospheric dispersion.

"Different regulatory activities require different models and model uses. The UK Environment Agency is a major user and instigator of the use of air dispersion models, to assess the impacts of airborne pollutants released from prescribed processes, in accordance with the Environmental Protection Act 1990. This assessment is a central feature of IPC (Integrated Pollution Control) and the BATNEEC (Best Available Techniques Not Entailing Excessive Cost) process and will continue to be so under IPPC (Integrated Pollution Prevention and Control) and BAT (Best Available Techniques).

Such calculations are formally required by the Agency for all permissions to operate. In the UK, there is no proscription (that is, the use of specific models) for regulatory studies and differences between dispersion calculations from different models and versions of models are then as important as their absolute veracity. The differences that exist in calculations between models and different versions of the same model are normally large enough to have a significant effect on regulatory decisions, which often involve substantial expenditure on commercial plant.

This problem has recently become more acute in the UK since the appearance of the USEPA's second generation AEROMOD model, which is now used alongside the UKADMS model, which had previously become a de-facto standard for regulatory work." (Hall 2001)

5.3.5. Information on the differences between models

Hall *et al* (2000) reviewed studies that had compared models, with emphasis on the extent to which models differed from one to another rather than on which model matched observed data most closely. Their objective was to elucidate the differences between models which can lead to significant differences in predicted exposure concentrations, since those results can become the basis for decisions that have important commercial implications.

The models compared included the traditional Gaussian model (Clarke, 1979) which was referred to as R91 (the NRPB report number for Clarke 1979). They also included another traditional Gaussian plume model used in the USA, the ISC model. Two CFD models were included: AEROMOD which is the standard CFD model used in the USA, and the UK ADMS. Several generations of the UK ADMS appeared in the various studies, so another factor can be difference between the generations of a given model.

In terms of the predicted concentrations, Hall *et al* noted that, for emissions from elevated sources such as stack emissions, the CFD models predict that the ground level concentration will start to rise closer to the stack than do the traditional Gaussian plume models. That could be an important difference in assessing the likely exposure to emission of nano-particles from industrial sources.

Assessing which model (or models) give predictions closer to the reality is a further step and is more difficult to assess because there are limited instances of the two models being applied to the same situation for which observational data are available, and the stochastic nature of the observations makes it difficult to determine which model gives best consistency.

5.4. Application of exposure models to estimate potential environmental exposure to engineered nanoparticles

5.4.1. Prediction of concentrations of engineered nanoparticles in soil and water

Data from Chapter 3 were used to derive usage inputs (Table 5.7) and the algorithms described in this Chapter were used to estimate potential concentrations of a range of ENPs in soil and water arising from use. These assessments focused on cosmetics and personal care products and paints as data were available on concentrations of a range of ENPs in these products. As only limited data were available on the fraction of each market comprised of ENP-containing products, three hypothetical scenarios were modelled:

1. the situation where 10% of a product type contains the engineered nanoparticle
2. the situation where half of a product type contains the engineered nanoparticle
3. the situation where all of a product type contains the engineered nanoparticle

We anticipate that, with the exception of sunscreens, all ENP containing products in the domestic sector make up less than 10% of market; scenario 1 therefore probably provides a conservative estimate of current environmental exposure. As an engineered nanoparticle can be used in a range of product types (e.g. C60 fullerenes could be used in a wide range of cosmetics), the potential environmental exposure resulting from multiple sources was also considered.

The results of the simulations are summarised in Table 5.8 and shown graphically in Figures 5.2 – 5.5. For the 10% market penetration scenario, concentrations of silver and aluminium engineered nanoparticles in water are predicted to be lower than 10 ng/l and fullerene C60 concentrations are predicted to be around 100 ng/l. Whereas, titanium dioxide, silicon oxide, zinc oxide, nanolatex and hydroxyapatite are predicted to be in the μg/l range. Predicted concentrations in soil range from 0.5 (aluminium oxide) to around 100 μg/kg (nanolatex). If all of these product types contain engineered nanoparticles in the future, then concentrations in water are estimated to range from 90 ng/l (aluminium oxide) to 1 mg/l (nanolatex).

These simulations assume that there are no other sources of the engineered nanoparticle of concern so it is important that they are updated as and when new information becomes available.

Table 5.7. Available data on concentrations of engineered nanoparticles in different product types

Product type	Engineered nanoparticle	Concentration (mg/g)
cosmetics and personal care products		
anti-inflammatory cream	fullerene clusters*	0.5
laundry detergents	latex$	5 - 100
eyeliner	fullerene C_{60}, C_{70} & C_{84}*	60
foundation	fullerene C_{60}, C_{70} & C_{84}*	1
Face powder	fullerene C_{60}, C_{70} & C_{84}*	1.5
lipstick	fullerene C_{60} & C_{70}*	3
mascara	fullerene C_{60} & C_{70}*	50
moisturizing vanishing cream	fullerene clusters*	0.5
perfume	fullerene clusters*	2.5
shampoo	Ag$	0.01 – 0.02
skin creams	fullerene $C_{60}$$	2.5
	Au$	3
soap	Ag$	0.01 – 0.02
sunscreen	$TiO_2$$	50
	ZnO$	155
toothpaste	hydroxyapatite$	150
	Ag$	0.01 – 0.02
paints and coatings		
paints	$Al_2O_3$$	0.5 - 5
	$SiO_2$$	15
	$TiO_2$$	5
	ZnO$	7-10
scratch resistant coatings	organo-silica*	10
scratch resistant wood coatings	ZnO*	2
	CeO_2*	1
biocidal coatings for construction materials	Ag*	0.001 – 0.1

* - product not thought to currently be in use in the UK; $- data indicates that products are available in the UK

Table 5.8. Predicted concentrations in sludge, soil and water for a range of engineered nanoparticles that are being used or could be used in cosmetics and personal care products and coatings. Predictions are presented for market penetration factors of 0.1, 0.5 and 1.0.

Particle type	Application	Water (µg/l)			Sludge (mg/kg)			Soil (µg/kg)		
		0.1	0.5	1	0.1	0.5	1	0.1	0.5	1
aluminium oxide	paint	0.0002	0.0012	0.0025	0.01	0.04	0.07	0.01	0.05	0.10
cerium dioxide	scratch resistant coatings	<0.0001	<0.0001	<0.0001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
fullerenes	anti-inflammatory cream	0.019	0.096	0.19	0.55	2.75	5.50	0.81	4.04	8.09
	eyeliner	0.0048	0.024	0.048	0.14	0.69	1.37	0.20	1.01	2.02
	face powder	0.071	0.36	0.71	2.04	10.18	20.4	2.99	15.0	29.9
	foundation	0.048	0.24	0.48	1.36	6.79	13.6	2.00	9.98	20.0
	lipstick	0.0023	0.011	0.023	0.06	0.32	0.64	0.09	0.47	0.95
	mascara	0.021	0.10	0.21	0.59	2.93	5.86	0.86	4.31	8.61
	moisturizing vanishing cream	0.024	0.12	0.24	0.68	3.39	6.79	1.00	4.99	9.98
	perfume	0.028	0.14	0.28	0.79	3.93	7.86	1.16	5.78	11.6
	skin cream	0.096	0.48	0.96	2.75	13.8	27.5	4.04	20.2	40.4
	total	**0.31**	**1.57**	**3.13**	**8.94**	**44.7**	**894**	**13.2**	**65.8**	**132**
gold	face cream	0.14	0.71	1.43	4.07	20.4	40.7	5.99	29.9	59.9
organo-silica	scratch resistant coatings	0.0005	0.0025	0.0050	0.01	0.07	0.14	0.02	0.10	0.21
silver	biocidal coatings	<0.0001	<0.0001	<0.0001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	shampoo	0.0063	0.032	0.063	0.18	0.90	1.80	0.26	1.32	2.65
	soap	0.0025	0.013	0.025	0.07	0.36	0.71	0.11	0.53	1.05
	toothpaste	0.0013	0.0067	0.013	0.04	0.19	0.38	0.06	0.28	0.56
	total	**0.010**	**0.051**	**0.10**	**0.29**	**1.45**	**2.90**	**0.43**	**2.13**	**4.26**
silicon oxide	paint	0.0007	0.0037	0.0074	0.02	0.11	0.21	0.03	0.16	0.31

Particle type	Application	Water (µg/l)			Sludge (mg/kg)			Soil (µg/kg)		
		0.1	0.5	1	0.1	0.5	1	0.1	0.5	1
titanium dioxide	paint	0.0002	0.0012	0.0025	0.01	0.04	0.07	0.01	0.05	0.10
	sunscreen	24.5	123	245	701	3504	7007	1030	5152	10305
	total	**24.5**	**123**	**245**	**701**	**3504**	**7007**	**1030**	**5152**	**10305**
hydroxyapatite	toothpaste	10.1	50.3	101	287	1436	2871	422	2111	4223
latex	laundry detergents	103	513	1025	2929	14643	29285	4307	21534	43067
zinc oxide	paint	0.0005	0.0025	0.0050	0.01	0.07	0.14	0.02	0.10	0.21
	scratch resistant coatings	0.0001	0.0005	0.0010	0.00	0.01	0.03	0.00	0.02	0.04
	sunscreen	76.0	380	760	2172	10861	21722	3194	15972	31944
	total	**76.0**	**380**	**760**	**2172**	**10861**	**21722**	**3194**	**15972**	**31944**

Figure 5.2. Predicted concentrations of fullerene C60 in water and soil

surface water
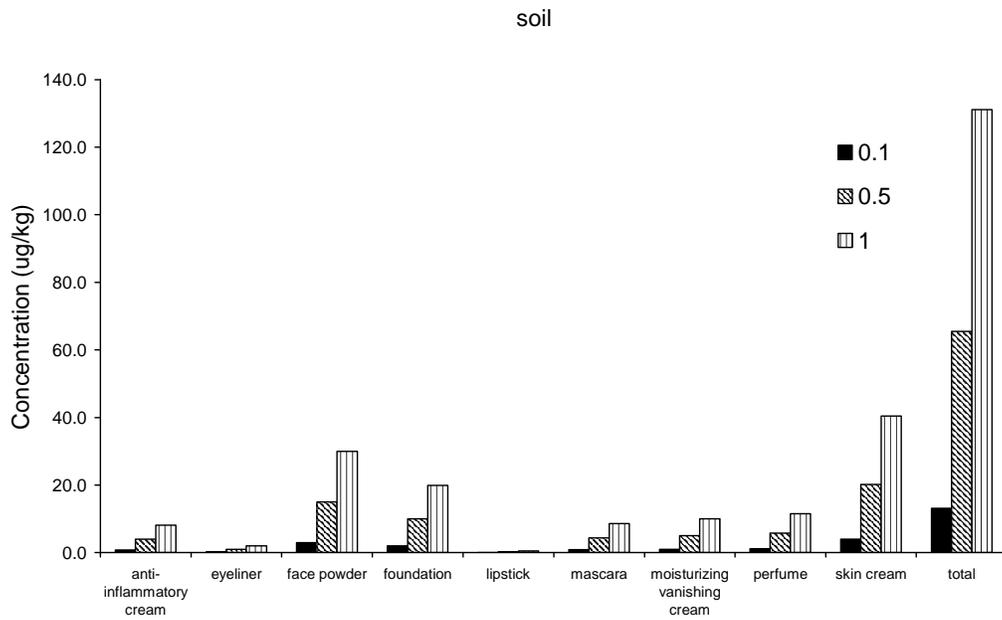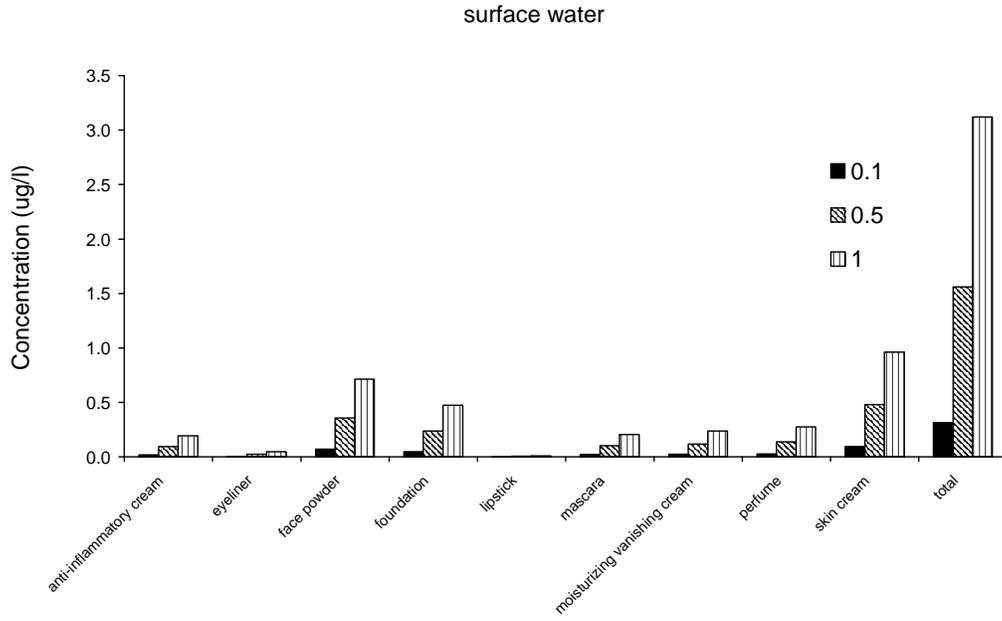
soil

Figure 5.3. Predicted concentrations of nano-silver in water and soil
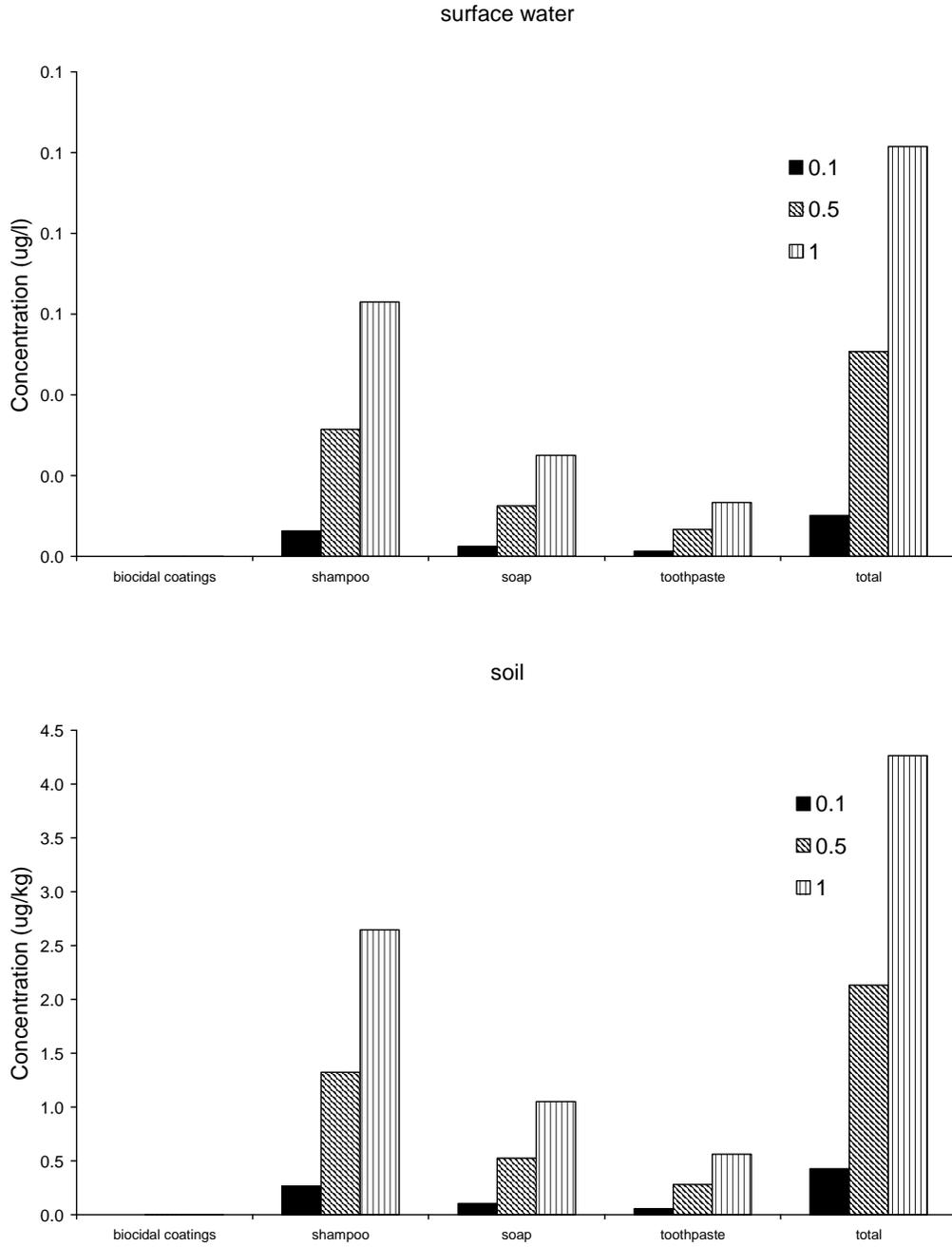
surface water

soil

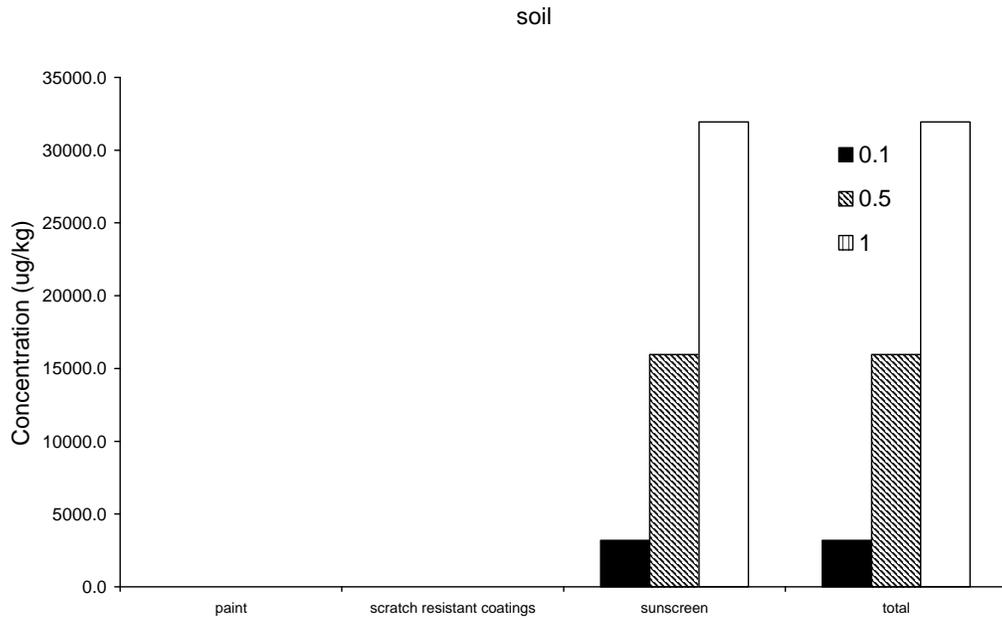**Figure 5.4. Predicted concentrations of zinc oxide ENPs in water and soil**
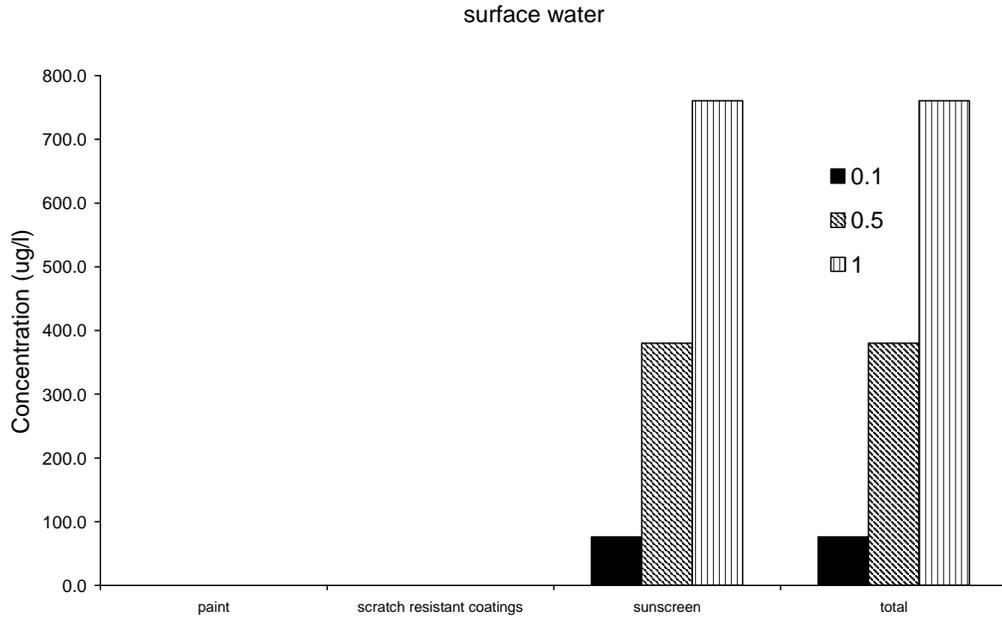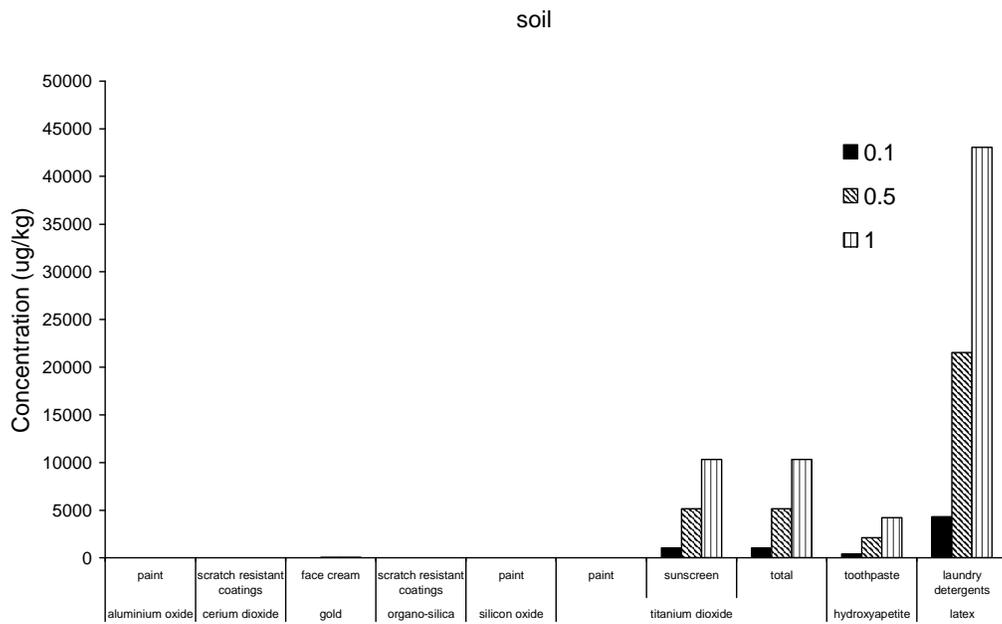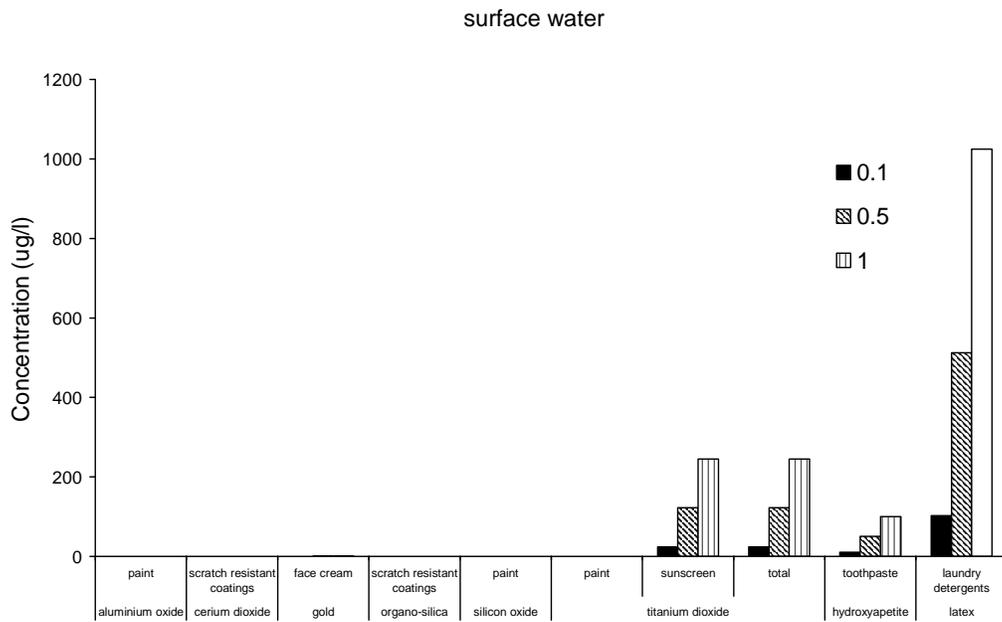
surface water

soil

Figure 5.5. Predicted concentrations of others ENPs in water and soil

surface water

soil

5.4.2. Prediction of aerial exposure arising from use of personal care products

Using the air exposure algorithms, it is also possible to assess exposure resulting from the use of personal care products.

If the consumer uses a 200 ml container of aerosol deodorant over approximately two months, then that is equivalent to about 3 ml per day. If we base the calculation on the presumption that the contents of the spray (propellant and active ingredients) has a unit relative density (i.e. density the same as that of water) then the quantity used is 3 gm per day, and assuming that is mainly from use once per day. If the nanoparticles are in the deodorant at the same concentration of 10 to 20 ppm as reported for soap (see Chapter 3), then *p* is approximately 0.00002. If there are 0.5 room changes per hour, then $k = 0.000139$. If it is assumed that 10% of the aerosol does not deposit directly on the skin but remains airborne, then *f = 0.1*. The concentration is then estimated at 0.006 mg/m^3 initially and would fall by about 8% in the ten-minute period.

Exposure to nanoparticles in spray-on sunscreen might be calculated similarly. Nanoparticle titanium dioxide has significant advantages for use in sunscreen, according to the manufacturer. For example, OPTISOL™ manufactured by Oxonica is microfine titanium dioxide incorporating a small amount (0.67%) of manganese in the crystal lattice. This allows absorbed UV energy to be dissipated, virtually eliminating the generation of free radicals. Manganese at the surface of the particle can scavenge free radicals that have been generated by other sunscreen components (Wakefield *et al* 2004).

According to the supplier's instructions on one brand of spray-on sunscreen that contains this ingredient, 200 ml of sunscreen should suffice for about 6 applications. That is consistent with the estimate earlier in this chapter, which suggested that about 30 g of sunscreen might be applied daily (to give a skin coverage of about 1 mg/cm^2 of skin). Then 5% of that may be the nanoparticle ingredient (e.g. nanoparticle TiO$_2$, Chapter 3), and if we again assume a fugitive spray emission as 10% (i.e. *p*=0.1), then that gives an estimate of the quantity of nano material *pfQ* emitted. If the spray sunscreen is applied indoors (so that the spray remains localised within say 4 m^3) the initial exposure concentration to nano material could be approximately 35 mg/m^3, based on the above assumptions. If the spray is applied outdoors then there would be more dilution, and an initial assumption might be that the spray is dispersed into the equivalent of 10 m^3 of air, and the concentration would be approximately 7 mg/m^3. If the proportion of fugitive emission of spray is of the order of 10% for some sunscreens, then this calculation indicates some non-trivial exposure concentrations, albeit probably for a short duration.

5.4.3. Emission of cerium oxide in vehicle exhausts

Presumptions

If cerium oxide is used at 10 ppm as an additive in all diesel (as estimated in the section 3.3), then an initial estimate of cerium oxide emission rate might be based on the presumption that it would amount to 10 ppm of the emissions from the diesel

fuel, i.e. the sum of the emitted hydrocarbon, the PM10 and the carbon component of emitted CO.

Example for emission rates

Estimates of emission rates (for pollutants such as PM10 but not cerium oxide) from vehicles are obtainable from the NAEI tools described in Section 5.3.2.   Those emission rates are given for various conditions of vehicles speed, traffic mix, and whether or not there are cold starts, and for specific classes of vehicle. .   For example, for:

- traffic flow at 40 km/hour,
- with no cold starts,
- at 1000 vehicles per day;
- and the traffic mix in Table 5.5.

The NAEI the emission rates for rigid heavy goods vehicles are PM 10 = 2.3 g/km, hydrocarbon = 8.0 g/km and carbon monoxide = 18.0 g/km.

Note that the NAEI tools call for an input specifying the number of per day, but later we need a vehicle flow in vehicles per hour.

Then, if we assume that the heavy goods vehicles are all diesels, and if all diesel contains cerium oxide at 10 ppm, this would give an estimate of the cerium oxide emission rate. The NAEI data gives emission rates for various classes of vehicle. For example, taking the rigid HGV (heavy goods vehicle), the cerium oxide emission rate would be estimated as $(2.3 + 8.0 + 18 \times 12/28) \times 10 / 1000,000 = 0.00018$ g/km. The traffic mix also includes articulated heavy goods vehicles, and buses and coaches. If we assume that they also are diesel and emit cerium oxide in the same way, then that can be added to the total.   Two further vehicle classes may contribute: diesel cars and diesel light goods vehicles (LGV). Including the data for those other classes gives a total cerium oxide emission of 0.0010 g/km for the passage of 1000 vehicles of the specified traffic mix.

The cerium oxide emission can be contrasted with the PM10 emission rate, which for the above example is 19.8 g/km. So, in this example, the emission rate of the cerium oxide would be approximately 0.00006 of the PM10 emission rate.

Further considerations

However, this estimation of proportion of cerium oxide in the emitted particles ignores the fact that modern vehicles may trap much of the particulate emission. That filtration may affect both PM10 and perhaps cerium oxide.

There is, of course a question as to whether the combustion process will have affected the state of the cerium oxide nanoparticles.   Laboratory studies have examined the effect of annealing temperature (298 to 973 °K) on the microstructure of cerium oxide nanoparticles. Ju *et al* (2005) used X-ray analysis to examine change in microstructure. They reported that X-ray scattering intensities increased dramatically as the annealing temperature went up to 873 K.

The cerium oxide used as fuel additives may also be doped with other constituents. For example, a US patent describes fuel additives which include particles of cerium oxide that have been doped with a divalent or trivalent metal or metalloid which is a rare earth metal, a transition metal or a metal of group IIA, IIIB, VB, or VIB of the Periodic Table (http://www.patentstorm.us/patents/7169196.html).

Estimated concentrations of cerium oxide in air

From the emission rate (for the relevant traffic conditions), the graph in Figure 5.1 can be used to estimate a concentration. The example above (traffic flow at 40 km/h, no cold starts, and defined traffic mix) gave an emission rate of cerium oxide at 0.0013 g/km for the passage of 1000 vehicles. If those vehicles passed in 1 hour, under otherwise identical condition (same speed, no cold starts), then that gives the emission rate of 0.0013 $g.km^{-1}.h^{-1}$.

In Figure 5.1, the concentration at 50 m from the road would be 0.02 $\mu g/m^3$ if the emission rate had been 1 $g.km^{-1}.h^{-1}$. As the emission rate (for this example of traffic) is 0.001 $g.km^{-1}.h^{-1}$ of cerium oxide concentration would be 0.0010 $\times$ 0.02 = 0.0002 $\mu g/m^3$.

At about 5 m from the road, the concentration would be three fold higher than at 50m. For this example, that would give a cerium oxide concentration of 0.0006 $\mu g/m^3$.

Annual emission of cerium oxide from vehicles in the UK

The estimated vehicle emission rates and the total annual mileage for vehicles in the UK gives a basis for estimating the overall emission of cerium oxide. The total vehicle kilometres was reportedly 500 billion in 2005, and 400 billion were by taxis and cars http://www.statistics.gov.uk/cci/nugget_print.asp?ID=1096. Thus about 100 billion kilometres were travelled by other vehicles. If those all emitted at the same rate as the vehicles with the highest emission factors (articulated heavy goods vehicles), then multiplying the cerium oxide emission rate estimated for those vehicles by the 100 billion km gives an estimate of 161 kg emitted. (This assumes that the mileage is stated in terms of American billions, which appears to be usual practice.) Actual consumption would be less than this estimate which is based on the worst case of all the distance (of goods vehicles) being travelled by the vehicle type with highest emission rate, and 100% market penetration of fuel with additive.

5.5. Expression of exposure in a metric most relevant to the potential effects.

5.5.1 Principle

Exposure to nano particles has been described in terms of quantity (mass) predicted as being likely to be present in the air, water or soil. However, the interaction with the environment may be related more closely to an alternative metric such as number or surface area of nano particles, and the method of measuring may need to be adapted to deal with the major differences in the reception of nanoparticles by the receptor, for example deposition of inhaled particles in the lung is strongly

dependent on particle size.   Application of control measures may reduce the potential exposure.   It will be important to take account of these effects in refinements of the modelling.

5.5.2 Exposure metric

To convert from an estimated mass exposure, based on consumption rates, to particle number or surface area of particles, will require information on particle size, and it may make a difference if the particles are aggregates or agglomerates. Aggregates (loosely bound collections of particles) or agglomerates (tightly bound collections of particles) may still be regarded as a nano-aerosol if the material retains all or some of its nano-scale properties (NIOSH, 2006).

In principle, predicted concentrations can be converted from one metric to another if the size distribution of the particles is known.   However, instruments are available that will give readings that enable alternative metrics to be obtained.   Some real time monitoring instruments will measure the number concentration of aerosols (by counting particles, with particle size being estimated from the amount of light scattered by the particle, other instruments measure surface area of the aerosol by using the electric charging properties of the particles and determination of the particle electrical mobility.   Specific surface area of fine dusts (in bulk) have been determined by gas adsorption measurements, for characterisation of samples for interpretation of toxicology tests.

5.5.3 Allowing for nano-particle-size dependent differences in deposition in the human lung

Deposition of particles in the human lung is dependent on the size of the airborne particulate.   Size selective sampling has been developed to exclude coarse particles that would not penetrate into the human respiratory tract.   There are accepted conventions for sampling inhalable dust (defined as dust that enters the nose or mouth), and for the sub-fractions that reaches the tracheobronchial region (thoracic or almost equivalently PM10) or the alveolar region of the lungs (respirable dust). However, the sampling conventions take into account only the loss of particles during inhalation (due to deposition, impaction, etc) and ignore the fact that some of the finer particles are exhaled.   For measuring mass concentrations of particles with mass median aerodynamic diameters greater than 1 µm, this has been a satisfactory approximation.   However, for particles with diameters in the nano range, the actual shape of the lung deposition curves needs to be taken into account.   There have been attempts to develop sampling instruments that would follow the lung deposition curves more closely (Kuo, Yu-Mei, 2005).   However, there are no such instruments commercially available currently.

Deposition will depend on the size of the aerosol particle.   For particles with diameter less than 300 nm, the deposition is produced by the thermodynamic process of diffusion or electrostatic attraction.   Diffusion is dependent on geometric size.   For particles with diameter greater than 0.3 µm (300 nm), the diffusion process is less important than inertial and gravitational deposition so that deposition is dependent on the diameter, shape (affecting aerodynamic resistance) and density (affecting inertia and gradational force).   Therefore, the deposition for particles larger than 300 nm (0.3 µm) can be expressed as a function of the *aerodynamic diameter*, which is defined as the diameter of the unit density sphere with the same gravitational settling speed as the particle.

The International Commission for Radiological Protection (ICRP) has published a human respiratory tract model for radiological protection (ICRP, 1994). The model is largely based on evidence from human volunteer studies that have characterised deposition of inhaled particles in the human respiratory tract, with the input of theoretical models to elucidate and extrapolate. For example, a theoretical model of hygroscopic growth was used to estimate the growth of such particles during inhalation and hence predict the deposition relative to the initial size of those particles. Breathing patterns are influential; for example a person breathing through the nose has less aerosol penetrating to the alveolar region than the habitual mouth breather. Therefore, the deposition in the lung is greater for the habitual mouth breather than for the nose breather. The example shown below in Figure 5.5 is for a person breathing through the mouth.

In Figure 5.6, showing an example of the ICRP model, both alveolar deposition and total deposition reach a minimum at about 300 nm. The curve for the alveolar deposition shows a substantial difference between the 0.13 for 300 nm particles and the 0.5 for 30 nm particles. That difference would not be reflected by the sampling convention for respirable particles, which would collect both of those particle sizes with approximately equal efficiency (ISO, 1993). That difference could be important, for example, if a nanomaterial aerosol could be released either as 30 or 300 nm aggregates, then nominally identical exposures to respirable dust concentrations (as measured by instruments complying with the sampling convention) would mask three fold differences in lung deposition and might lead to apparently contradictory evidence on health effects.

5.5.4 Effectiveness of control measures.

Filtration on exhaust ventilation

It is also important to assess the extent to which control measures are to be expected to be effective in preventing release of nano aerosols. Where filtration operates primarily by impaction, then it is likely to be much less effective against nano particles than against particles greater than 1 μm (1000 nm). However, High Efficiency Particle Air (HEPA) filters are expected to be effective against nanoparticles. NIOSH (2006) cited Hinds (1999); the HEPA filters are tested with particles of a size (300 nm) expected to give the lowest capture efficiency. This is the particle size which shows least capture in the lungs (Figure 5.6) for the same reasons; at larger size the inertial capture becomes predominant, and at lower sizes the thermodynamic (diffusional) capture becomes predominant.

Figure 5.6 illustrates the dependence of disposition on particle size for the example of an adult male who is a habitual mouth breather, data from the ICRP model (Table F.1 of that publication).
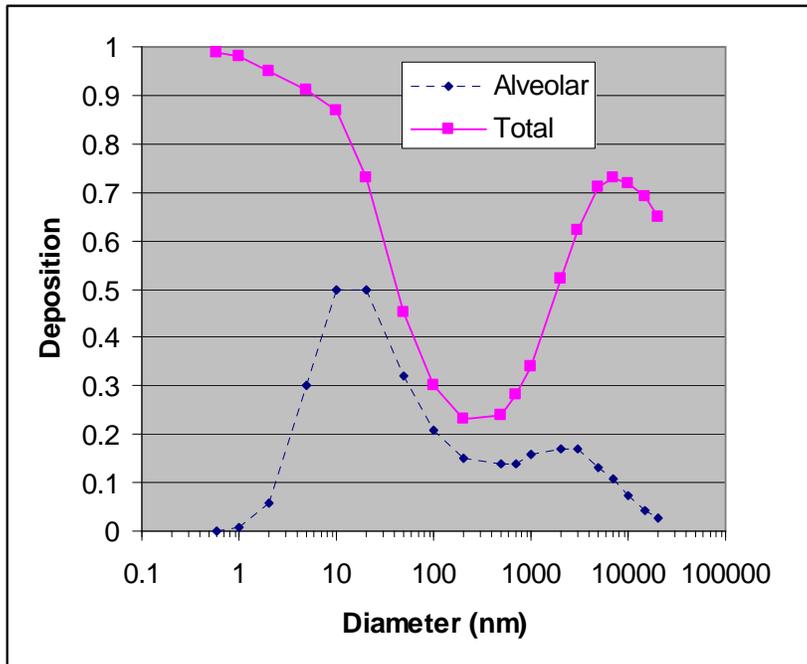
Electret filters

Some filters, e.g. electret filters, which utilise electrostatic forces may have a minimum effective particle size around 50 nm, as those much smaller particles are more likely to carry no net electric charge. These filters can include respirator filters. For that reason, there is ongoing work at NIOSH in the USA (NIOSH (2006) to assess the efficacy of filters against nanoparticle aerosols.

Diesel exhaust filtration

Some modern diesel engines are fitted with filters as part of the exhaust system. The web site of one supplier describes how the filters work. *The most effective and practical method is by using a ceramic filter substrate, usually silicone carbide with micro-porous walls. This traps the solid particles, allowing the gases to escape through the wall and hence vent into the exhaust outlet.*

The collected soot builds up within the filter, which will clog and eventually block resulting in a build up of engine back pressure unless it is removed, which is achieved by a process known as regeneration. Regeneration is achieved by burning the collected soot within the filter, either actively or passively. In an active system a separate, usually electrical, heat source is applied to raise the temperature to a point where the carbon particles are burnt off to produce CO_2. In the passive system the

heat of the engine exhaust gas is used in conjunction with a special catalytic coating on the filter to achieve the same result.

Cerium oxide has a high melting point approximately 2100 °C, and a boiling of about 3500 °C. Therefore, it may be left as an incombustible residue on the ceramic filter. If so, then filtration within vehicle exhaust systems might prevent release of the cerium oxide. It will be important to verify what happens to the cerium oxide during active and passive regeneration of filters. Model predictions (of likely exposure) would need to be adjusted to allow for the proportion of vehicles fitted with such filters and the filtration efficiency of the filters.

6. Discussion and Recommendations

Nanotechnology is a rapidly expanding area and engineered nanomaterials/nanoparticles (ENPs) are finding applications in a wide range of areas including use in cosmetics, bioremediation and water treatment (e.g. Aitken *et al.*, 2006; Kamat and Meisel, 2003; Savage and Diallo, 2005). It is therefore inevitable that during their manufacture and use, ENPs will be released to the environment. This study was therefore performed to 1) identify the potential releases of ENPs to the environment; 2) review the fate of ENPs in environmental systems and 3) to assess the potential current and future environmental exposures.

Whilst ENPs may be emitted during the manufacturing process, the route of input to the environment will primarily depend on the end use of the ENP-containing product. For example, pharmaceuticals, cosmetics and sunscreens may be emitted to the sewage system following excretion from the patient or during washing and showering. Once they have passed through the sewer system they may be released to surface waters. Sunscreens and other cosmetics applied on skin may also enter surface waters directly during swimming or bathing. Waste cosmetics are most likely to be disposed of in household waste that may be land filled or incinerated. Paints containing ENPs can have both industrial and domestic uses. It is possible that run-off from painted surfaces and domestic use of paints could result in discharges to sewers. In instances where paint is applied to underwater structures or ships, ENPs may be released directly to surface waters. The use of ENPs in fuel and catalysts in vehicles will result in direct aerial emission of particles through vehicle exhaust or emissions to the surface waters and sewers through leakage and spills. Waste lubricants are most likely to be disposed of as special waste that may be land filled or incinerated. The use of nanoparticles in treatment of polluted water is likely to result in direct emissions to surface and groundwaters or soil. ENPs used to deliver agrochemicals will be released directly to soils and surface waters.

A number of products that contain ENPs have been identified that are currently on the UK market (see Chapter 3). However, due to a lack of published data, it is not currently possible to estimate the UK market penetration for these products. Moreover, whilst some data are available on the concentrations of ENPs in selected products, for some products this is totally lacking.

Over the past few years there has been increasing interest in the environmental behaviour of ENPs. Chapter 4 has reviewed a number of studies that have investigated the fate and transport of ENPs in environmental systems. However, whilst it is clear that these studies have generated useful knowledge on the behaviour of ENPs in air and water systems, we know nothing about the fate of ENPs in sewage treatment systems and the interactions of ENPs with suspended solids, sediments and soils. In water and soil systems, there is also a wealth of data available on the behaviour and transport of natural colloids that could provide useful information on ENP behaviour.

Available data indicate that, following release to water and air, nanoparticles will aggregate to some degree and that the behaviour of the resulting aggregates will be very different from the free nanoparticle The degree of aggregation and the size

range of the aggregates is dependent on the characteristics of the particle (e.g. type, size, surface properties and, for magnetic metal particles, the intrinsic magnetic moment), the concentration of the particles and the characteristics of the environmental system (including pH, ionic strength and dissolved organic carbon content). It is important to recognise that many ENPs may be functionalised to improve efficacy and that this functionalisation could significantly affect particle behaviour. Care should therefore be employed when assessing the risk of ENPs to ensure that the correct particle type is being assessed. Environmental transport studies indicate that ENPs will exhibit differing mobilities in the soils and waterbodies and in water treatment processes compared to their corresponding parent form. Selected NPs have been shown to have the potential to contaminate aquifers (Lecoanet *et al.*, 2004) and pass through water treatment processes (e.g. Westerhoff *et al.*, unpublished data), although the behaviour varies depending on nanomaterial type (Lecoanet *et al.*, 2004). The behaviour of nanoparticles in environmental systems is therefore highly complex and appears to be dependent on not only the particle type but also the particle size and the nature of the receiving environments. Models may provide a way to address this complexity for risk assessment purposes.

A number of modelling approaches have been proposed for predicting behaviour of ENPs in the aquatic environment (Mackay *et al.*, 2006). however these have yet to be fully evaluated for their applicability to natural systems. The behaviour of colloidal material in the soil environment has also been extensively studied and models have been developed for predicting behaviour (e.g. Grolimund *et al.*, 2001; Dunphy Guzman *et al.*, 2006). As engineered nanoparticles may be of similar size to colloids, it is possible that these approaches could be applied to predict the behaviour of ENPs in the soil environment. However the extent to which engineered nanoparticles behave differently to colloids has yet to be established. Exposure models for assessing fate in sewage treatment systems (e.g. ToxChem), surface waters (e.g. TOXSWA and GREATER) and fate and transport in the soil environment (e.g. PEARL, PRZM and MACRO) are available and are used in the risk assessment of conventional chemical contaminants (e.g. pesticides, industrial chemicals). However these typically require information on the environmental fate characteristics of a substance (including sorption behaviour and persistence) and again have not been evaluated for their applicability to ENPs.

Due to the lack of knowledge on ENP fate and behaviour in the environment and uncertainty in the applicability of the above models, we have proposed a framework of simplistic models and algorithms that could be used to estimate concentrations in water, soil and air. The models do not consider degradation and interactions with soil, sediment etc but are likely to provide conservative estimates of exposure concentrations. Due to their simplicity, the models provide no information on the characteristics (e.g. likely particle size distribution or surface properties) of the ENPs in the environmental compartment of interest. Nevertheless we believe that the outputs of these models will be invaluable in a) guiding future development of analytical methodologies by providing information on likely detection limits that will be required; b) prioritising ENPs for further research; c) informing the design of environmental fate studies by providing information on the concentration ranges that should be studied; and d) interpreting environmental toxicology data (this will be discussed later.

Using the information in Chapter 3, the modelling framework was applied to estimate the likely concentrations of ENPs in the UK environment. For the 10% market penetration scenario, which probably overestimates current exposure, concentrations of silver, aluminium and fullerene C60 concentrations were predicted to be in the ng/l. Whereas, titanium dioxide, zinc oxide, nanolatex and hydroxyapatite are predicted to be in the μg/l range (Table 6.1). Predicted concentrations in soil range from <0.01 (cerium dioxide) to around 4.3 mg/kg (nanolatex). By combining these predictions with the results of experimental fate studies, it is possible to generate an indication of the potential level exposure and the form of the exposure (Table 6.1). These exposure concentrations assume complete release to the environment, do not consider removal in treatment processes or removal in the environment (e.g. due to sedimentation) so are probably highly conservative although it is also important to recognise that many NPs may also exist naturally (e.g. Diallo *et al.*, 2005) or be formed in the water bodies (e.g. Nagy *et al.*, 2003) or be released to the environment in mine wastes (e.g. Walker *et al.*, 2005; Waychunas *et al.*, 2005) and that these natural sources may add to the exposure of many ENPs.

Table 6.1. Summary of exposure data for selected ENPs in the UK environment (assuming 10% market penetration)

	Water (μg/l)	Soil (μg/kg)	Air (mg/m^3)	Aggregate size (nm) in water mean and range
Ag	0.010	0.43	-	-
AlO$_3$	0.0002	0.01	-	-
Au	0.14	5.99	-	-
CeO$_2$	<0.0001	<0.01	6×10^{-7}	-
fullerenes	0.31	13.1	-	75 (25-500)
hydroxyapatite	10.1	422	-	-
latex	103	4307	-	-
organo-silica	0.0005	0.02	-	-
SiO$_2$	0.0007	0.03	-	205 (135-510)
TiO$_2$	24.5	1030	7	330 (175-810)
ZnO	76	3194	-	480 (420 – 640)

The exposure data developed in this study provide a benchmark against which existing ecotoxicology data on ENPs can be compared. A number of studies have explored the uptake and effects of nanoparticles on a range of environmental species and endpoints (Oberdorster, 2004, Lovern and Klapper, 2006, Oberdorster *et al.*, 2006; Kashiwada, 2006). In the laboratory, aquatic organisms appear to rapidly accumulate selected nanoparticles, including carbon black, titanium dioxide and polystyrene (e.g. Lubick, 2006, Stone *et al.*, 2006).

Laboratory studies with microbes have reported effects of fullerenes on microbial physiology (e.g. Fortner *et al.*, 2005, Fang *et al.*, 2007) whilst silver nanoparticles have been shown to accumulate in bacterial membranes, ultimately causing cell death (Sondi and Salopek-Sondi, 2004). In some cases there is however a mismatch between laboratory studies and studies to assess impacts in the real environment. For example, under realistic exposure conditions, fullerenes have little impact on the structure and function of the soil microbial communities and microbial processes (Tong *et al.*, 2007).

The available data indicate that nanoparticles have low acute toxicity to aquatic organisms (e.g. Lovern and Klaper, 2006, Oberdorster *et al.*, 2006, Zhu *et al*, 2006) although they may cause oxidative stress and affect the physiology and reproduction (Lovern and Klaper, 2006, Oberdorster *et al.*, 2006, Templeton *et al.*, 2006)(Table 6.2). Studies with algae have demonstrated that titanium dioxide nanoparticles inhibit algal photosynthesis (Kim and Lee, 2005). Studies with fish have demonstrated oxidative stress in the brains of fish exposed to fullerenes at very low concentrations (Oberdorster 2004). Although there is some debate over whether the effects were caused by the fullerenes or the carrier solvent. Studies with plants have shown aluminium nanoparticles to inhibit plant growth.

A comparison of the results of the exposure estimations with the available ecotoxicological data (Table 6.3) is reassuring and indicates that even the conservative exposure concentrations generated in this study are many orders of magnitude lower than concentrations likely to cause acute effects or subtle effects on invertebrates or bacteria.

Table 6.3. Summary of exposure data for selected ENPs in the UK environment (assuming 10% market penetration)

	Water (µg/l)	Invertebrate EC50 (µg/l)	Fish LC50 (µg/l)	Algae EC50 (µg/l)	Other endpoints
C_{60}	0.31	> 35000	>>5000	-	effects on invertebrate behaviour at 260 µg/l; bacterial growth effected at 40 µg/l; bacterial phopholipid effected at 10 µg/l
TiO_2	24.5	>100,000	>100,000	16,000	effects on invertebrate behaviour at 2000 µg/l; bacterial growth not effected at 100000 µg/l
SiO_2	0.0007	-	-	-	no effect on bacterial growth at 500000 µg/l
ZnO	76	-	-	-	no effect on bacterial growth at 10000 µg/l

6.1. Conclusions

It is inevitable that during their use ENPs will be released to the environment. The potential for environmental exposure will be determined by the amounts of different ENP-containing products used, the pattern of use and the concentration of ENP in each product. Whilst information on the environmental fate of ENPs is limited, once in the environment the ENPs are likely to aggregate. This will affect the properties and mobility of the particles. The behaviour in the environment is complex; it is affected by a range of particle properties and the physical and chemical characteristics of the receiving environment. As usage and fate data are limited, a simplistic modelling framework has been proposed for developing conservative estimates of ENPs in a range of environmental compartments. This framework has been applied to a range of product types and has provided an indication of what the level of exposure might be now and in the future. Comparison of these predictions with available acute and sublethal ecotoxicological data indicate that even using highly conservative estimates of exposure, concentrations in the environment are

likely to be considerable lower than concentrations required to produce toxicological effects. There are however, significant gaps in our knowledge that need to be addressed before risks can be fully established. Recommendations for future work are therefore provided below.

6.2. Recommendations for future work

It is clear from this study that there are significant gaps in our current knowledge regarding the use, environmental fate and exposure of ENPs in the UK environment. We would therefore advocate that work in the future focuses on the following areas:

1. The development and maintenance of an inventory of which products in use in the UK contain ENPs, the concentrations of the ENPs within the products and on the specific characteristics of ENPs used in these product (non-functionalised vs functionalised, size, shape etc.). Defra currently have a voluntary reporting mechanism for ENPs in use in the UK so a mechanism is already in place to obtain this information.
2. The development of emission scenarios for ENPs at different stages of a product life cycle. In this project we have assumed that inputs from the manufacturing process and disposal are minimal compared to inputs during use. Moreover we have only been able to develop usage scenarios for selected product types.
3. Studies to explore the fate and behaviour of ENPs in a range of environmental systems (wastewater treatment, surface waters, soil and air). Whilst knowledge of some fate processes in some compartments is fairly well developed, knowledge of many systems and processes is limited or totally lacking. There is therefore an urgent need to develop an understanding of those factors and processes affecting the fate of ENPs in natural systems. Particular attention should be paid to wastewater, soil and sediment and to the persistence and sorption behaviour. Effects of important environmental variables such as humic substance concentration and the effects of particle modification on fate and behaviour of ENPs should also be studied.
4. Based on the information obtained from the types of studies described above, models for more accurately predicting concentrations of ENPs in natural systems should be developed. These models should not only estimate exposure concentrations but also the characteristics (size, shape, surface properties) ENPs are likely to adopt in the natural environment. It is possible that existing environmental exposure models could be adapted using models from other disciplines (e.g. colloid science) to achieve this.
5. The development and validation of analytical methods for measuring ENPs in the natural environment. Ultimately, these approaches should be used for environmental monitoring purposes and the evaluation of exposure model.
6. Ecotoxicity and environmental fate investigation should be performed in a more integrated manner. It is clear that the behaviour of ENPs in environmental systems is complex and can be very different from behaviour in simple laboratory systems (as used in most ecotoxicity studies). For risk assessment purposes, it is very important that ecotoxicological studies consider the potential effects of the form of the ENP that is likely to occur in the environment.
7. The models proposed in this study and/or more sophisticated models should be constantly applied, as new information becomes available, to assess the potential exposure arising from ENPs.

8. As many ENP are likely to be used in a range of product types and the environment will be exposed to all of these, it is essential that all potential sources are considered in future risk assessments

Table 6.2. Available ecotoxicity data for a range of engineered nanoparticles

ENP	Test species	Endpoint	Result (mg/L)	Reference
fullerene C60	Daphnia magna	48 h LC50 (mortality)	>35 for water stirred C60 0.8 for THF applied C60	Zhu *et al.*, 2006
	Daphnia magna	hopping, heart rate appendage movement	effects observed at 0.26 mg/l	Lovern *et al.*, 2007
	Daphnia magna	21 d mortality, reproduction and moulting	40% mortality observed at 35 mg/l; effects on moulting and reproduction observed at 2.5 mg/l	Oberdorster *et al.*, 2006
	Hyallela azteca	96 h mortality	no effect at 7 mg/l	Oberdorster *et al.*, 2006
	copepods	96 h mortality	no effect at 22.5 mg/l	Oberdorster *et al.*, 2006
	Pimephales promelas	96 h mortality and sublethal effects	no mortality at 0.5 mg/l; PMP70 protein expression suppressed at 0.5 mg/l but no effect on CYP 1A, 2M1 and 2K1 levels	Oberdorster *et al.*, 2006
	Oryzias latipes	96 h mortality and sublethal effects	no mortality at 0.5 mg/l; no effect on CYP 1A, 2M1 and 2K1 PMP70 protein levels at 0.5 mg/l	Oberdorster *et al.*, 2006
	Escherichia coli	growth	no growth at 0.4 mg/l; growth at 0.04 mg/l	Fortner *et al.*, 2005
	Escherichia coli	respiration	inhibition at 4 mg/l; no inhibition at 0.4 mg/l	Fortner *et al.*, 2005
	Bacillus subtilis	growth	no growth at 0.4 mg/l; growth at 0.04 mg/l	Fortner *et al.*, 2005
	Bacillus subtilis	respiration	inhibition at 4 mg/l; no inhibition at 0.4 mg/l	Fortner *et al.*, 2005
	Bacillus subtilis	phospholipids and membrane phase behaviour	effects observed at 0.01 mg/l	Fang *et al.*, 2007
	Bacillus subtilis	minimal inhibitory concentration	nC60 = 0.4 − 0.6 mg/l; 'small' nC60 particles = 0.1 − 0.23; 'large' nC60 particles = 0.75 − 1.5	Lyon *et al.*, 2006
	Pseudomonas putida	phospholipids and membrane phase behaviour	effects observed at 0.01 mg/l	Fang *et al.*, 2007

ENP	Test species	Endpoint	Result (mg/L)	Reference
	soil microbes	community structure and function	little effect at 1 mg/kg (nC60) and 1000 mg/kg (C60)	Tong *et al.*, 2007
TiO$_2$	*Oncorhyncus mykiss*	96 h LC50 (mortality)	>100	Warheit *et al.*, 2007
	Daphnia magna	48 h EC50 (immobilisation)	>100	Warheit *et al.*, 2007
	Pseudokirchneriella subsapitata	72 h EC50 (growth)	16	Warheit *et al.*, 2007
	Daphnia magna	hopping, heart rate appendage movement	no effects observed at 2.0 mg/l	Lovern *et al.*, 2007
	Bacillus subtilis	growth inhibition	no inhibition at 500 mg/l; 75% inhibition at 1000 mg/l	Adams *et al.*, 2006
	Escherichia coli	growth inhibition	no inhibition at 100 mg/l; 15% inhibition at 500 mg/l	Adams *et al.*, 2006
SWNTs	*Amphiascus tenuiremia*	28 – 35d EC50 (mortality, development, reproduction)	> 10 (effects on mortality, fertilization and moulting rates observed at 10 mg/L)	Templeton *et al.*, 2006
	Oncorhyncus mykiss	10 d sublethal effects	effect on respiration at 0.1 mg/l; no major disturbance to haematology; changes in brain and gill Zn and Cu; increase in Na$^+$K$^+$-ATPase	Smith *et al.*, 2007
LPC-SWNTs	*Daphnia magna*	96 h mortality	100% mortality at 20 mg/l; 20% at 10 mg/l; no mortality at 5 mg/l	Roberts *et al.*, 2007
C60HxC70Hx	*Daphnia magna*	hopping, heart rate appendage movement	effects observed at 0.26 mg/l	Lovern *et al.*, 2007
SiO$_2$	*Bacillus subtilis*	growth inhibition	no inhibition at 500 mg/l; 7% inhibition at 1000 mg/l	Adams *et al.*, 2006

ENP	Test species	Endpoint	Result (mg/L)	Reference
	Escherichia coli	growth inhibition	no inhibition at 100 mg/l; 15% inhibition at 500 mg/l	Adams *et al.*, 2006
ZnO	*Bacillus subtilis*	growth inhibition	90% inhibition at 10 mg/l	Adams *et al.*, 2006
	Escherichia coli	growth inhibition	14% inhibition at 10 mg/l	Adams *et al.*, 2006

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Glossary

BOD   Biological oxygen demand

CFD   Computational fluid dynamics

EC50   Median effective concentration

EDC   Endocrine disrupting chemical

ENP   Engineered nanoparticle

EPS   Extracellular polymers

FOG   Fats, oils and greases

HDV   Heavy duty vehicle

HEPA   High efficiency particle air

LC50   Median lethal concentration

LDV   Light duty vehicle

MBR   Membrane bioreactor

NAEI   National atmospheric emission inventory

NRCG   Nanotechnologies Research Co-ordination Group

OSPM   Operational street pollution model

PEC   Predicted environmental concentration

SWNT   Single walled carbon nanotube

ZvFe   Zero valent iron